QATAR UNIVERSITY

COLLEGE OF ENGINEERING

PHOTOBIOREATOR TECHNOLOGY FOR CARBON CAPTURE AND NUTRIENTS REMOVAL

BY

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A Thesis Submitted to the Faculty of

the College of Engineering

in Partial Fulfillment

of the Requirements

for the Degree of

Masters of Science in Environmental Engineering

June 2017

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ABSTRACT

SHURAIRE, MOHAMMED, S., Masters : June : [2017:], Masters of Science in Environmental Engineering

Title: Photobioreactor Technology for Carbon Capture and Nutrients Removal

Supervisor of Thesis: Fares, A.O, AL Momani.

Carbon dioxide concentration in the atmosphere is increasing significantly worldwide. Many are debating the influence of increasing carbon dioxide concentration on global climate, but most scientists agreed that the increasing carbon dioxide concentrations will have a deep effect on the environment. Most of the carbon dioxide results from combustion of fossil fuels to fulfill the increasing demand for energy. Meeting this demand without significantly increasing the Carbon dioxide emissions will require more than the conventional carbon capture and storage techniques. There is growing recognition of microalgae as one of the most efficient biological systems to capture industrial CO_2 and produce biomass (bio-fuel) at the same time. Algae also has the potential to remove nutrient from wastewater such as nitrogen and phosphorus. Green algae utilize carbon dioxide in their main building blocks in the photosynthesis process, which means that algal have a high potential for CO_2 capture and sequestration. Algae can also produce high value products which can boost the revenues to overcome the relatively expensive microalgae culturing. Algae requires sunlight and CO_2 to perform the photosynthesis process, to maximize the energy stored in algae and increase the growth rate of algae a large amount of CO_2 is required which is available from the discharge of heavy industries. Algal production does not require a high purity CO_2 stream, flue gas containing different CO_2 concentrations can be fed directly to the photo-bioreactor which will make the CO_2 separation from the flue gas much easier and less expensive. The objectives of the study were (1) evaluate the capability of algae to

capture CO_2 from gaseous streams at different concentrations [5, 10and 15v/v%] and different temperatures [20, 25, 30°C], (2) ability of algae to remove nutrient from secondary effluent wastewater under different temperatures [25 and 30°C], and CO_2 concentrations [5% and 10%]. Experiments were carried out in lap-scale and pilot scale set up. Lab-scale results showed that the maximum growth rate, biomass productivity and CO_2 bio-fixation rate for *Spirulina platensis* (SP.PL) were obtained at temperature of 25°C for culture injected with 10 v/v% CO_2. Under these conditions, growth rate, biomass productivity and CO_2 bio-fixation rate were determined to be 0.772 d^{-1}, 0.15 $g.L^{-1}.d^{-1}$ and 0.281 $g.L^{-1}.d^{-1}$, respectively. These values are higher than the values reported in literature for green algae strains grown under similar conditions. Higher growth rate, biomass productivity and CO_2 bio-fixation rate were obtained in the experiments carried out using natural solar light in pilot plant PBR. SP.PL under the same previous conditions (25°C and 10% CO_2 injection) was able to achieve biomass productivity and CO_2 biofixation rate of 0.153 $g.L^{-1}.d^{-1}$ and 0.281 $g.L^{-1}.d^{-1}$, respectively. Experiments carried out to study the performance of SP.PL in removing nutrients from wastewater showed a typical algae growth rate under both temperatures (25 and 30°C) and CO_2 injection dosage (5 and 10%). The growth of algae in wastewater was observed to have lag phase up to 7 days followed by an exponential growth phase. Decay or stationary phase was not observed under the tested operational conditions. Ammonia removals by SP.PL for experiments performed at 25 ◦C and with CO_2 injection of 0, 5 and 10 % were 94.5, 92.4 and 84.5%, Respectively. The % phosphorous removals for the same previous conditions were 94.8, 89.3 and 84.2%, respectively. The results of this study show that microalgae-based wastewater treatment systems can be successfully employed at different temperatures as a successful CO_2 capturing technology and post-wastewater treatment process.

ACKNOWLEDGMENTS

I would like to express my gratitude and sincere appreciation to my supervisor Dr. Fares Al Momani for his continuous support during this study. Special thanks to Mr. Khalid Al Jaml for the unlimited support during the experimental work of this study. Special thanks also to my best friends Abdulrahman, Khalid and Mustafa it was an amazing journey and finally I would like to thank my family for the continuous encouragement and support.

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Chapter 1: Introduction

1.1 Research Description:

Microalgae, wastewater and renewable solar light can solve both economic and environmental problems when utilized efficiently in an engineered photo-bioreactor. Where the CO_2 is bio-captured, wastewater can be treated and more algae can be produced and converted into biofuels or other useful chemical). Microalgae under specific conditions (light intensity, temperature and pH) can utilize low-quality water as growth medium in the presence of nitrogen (N), phosphorus (P) and minor nutrients which can be used for algae growth. Nevertheless, there are many challenges that hinder the successful scale up of such technologies to be economically feasible. The challenges are related to the impact of light intensity (low or high) on the growth of algae; excess light intensity sometimes leads to photo-inhibition and light saturation effect. Accumulation of oxygen in the growth medium and the high temperature inside the photo-bioreactor caused by the high solar radiation operating in summer periods particularly during midday light hours in Qatar would lead algae to stop photosynthesis and growth. the influence of wastewater quality on the CO_2 and nutrients uptake rates under natural solar light. The main objective of this study is to investigate the potential of green algae as a CO_2 capturing technology and wastewater treatment process.

1.2 Objectives:

The major objective of this study is to evaluate the potential use of microalgae as a wastewater treatment technology and CO_2 capturing. The following specific objectives in meeting this major aim will be thoroughly investigated:

1. Investigate the capacity of Spirulina platensis for CO_2 bio-capturing under different CO_2 dosage and temperatures.
2. Study and evaluate the performance of SP.PL as advanced wastewater treatment for nutrient removal.
3. Monitor the growth rate of SP.PL under different operation conditions (light, CO_2 loading, and temperature) to establish optimal growth conditions.
4. Investigate the performance of photo-bioreactor under natural sunlight. Specifically, the influence of light intensity and temperature on CO_2 bio-capturing rate and biomass growth rate.

1.3 Thesis Organization

In Chapter 2, the literature was reviewed to present all the available information about CO_2, Algae and photobioreactors. Chapter 3 presents the materials and methods used during the experimental testing. Chapter 4 presents the obtained experimental data and discussions for CO_2 capture in lab-scale reactor, CO_2 capture in pilot plant and nutrients removal from wastewater.

Chapter 2: Literature Review

2.1 Introduction:

Scientific evidences show that the earth's climate is significantly affected because of the continuous emissions of greenhouse gases (GHGs). Rising CO_2 level in the atmosphere leads to global warming as CO_2 is one of the potential GHGs. Figure 2.1 shows the main sources of CO_2 produced in the United States. As it can be seen in the figure the leading sector in producing CO_2 is the electric power generation; it was estimated that this industry contributes to 39.8% of the global CO_2 emission. Transportation sector comes in the second place with an emission percentage of 33.5%, followed by the industrial sector with 15.9%.

As per the Inter-Governmental Panel on Climate Change (IPCC) report 50-80% of global CO_2 emissions must be cut to reverse the most harmful effects on our climate (Ipcc, 2014). Several projections indicate that the need for fossil fuels will continue to increase.

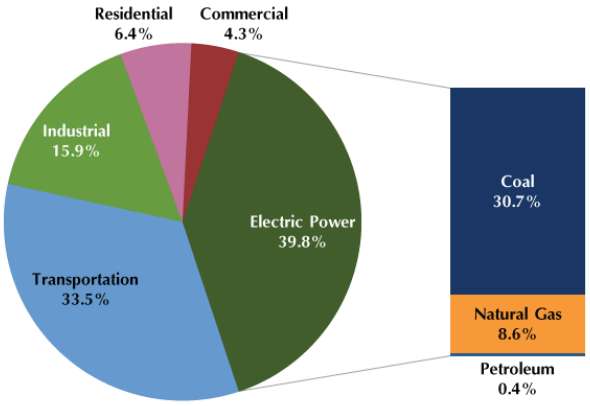

Figure 2.1 : CO_2 sources in the United States (Administration, 2015, EPA, 2014)

It is acknowledged that Qatar and most of the GCC countries have the highest per capita carbon footprint worldwide (Table 2.1), and these countries are in need for the implementation of carbon capture and carbon utilization technologies.

Table 2.1 : United Nations, Qatar CO_2 emissions per capita.

indicator	*Global Rank*	*Global share*	*Notes*
CO_2 emissions from fuel combustion (2012)	43	0.24%	75.8 Mt CO2 Eq.
Population (2013)	142	0.03%	2.17 Million
CO_2 emissions / Pop. (2012)	1		36.95 tCO_2 per capita
GDP Size (2013)	49	0.28%	
UNDP human development index (2012)	36		
GDP Structure% - Share of GDP (2013)	- Imp: 29, Exp 76		

The primary sources of energy in Arab gulf countries is fossil fuels, mainly refined petroleum products and natural gas and GHGs emitted from the energy sector are mostly CO_2. Figure 2.3 shows the CO_2 emission in the state of Qatar reported by Ministry of Environment as of year 2011. The Arab Gulf countries, with largest reserves of fossil fuels in the world and the largest per capita emission of GHGs, use 90% of its energy for Oil & Gas, manufacturing, electricity and water desalination. In this arid region with high climatic variability, any further climatic change could produce large effects on the eco-systems and environment. Climate records in these

countries show that the annual mean temperature has increased by 0.3ºC over the last 40 years. The Arab Gulf countries are members of international environmental treaty, and are committed to submitting national communications on measures and initiatives in response to the challenge of climate change. It is worthy to note that recently these countries have started several voluntary initiatives to address the climate and sustainable development goals. The outcome of this treaty is the joint research project between industries and academic institutions concentrating in Carbon capture and storage (CCS) technologies ($70 million and for 10-year).

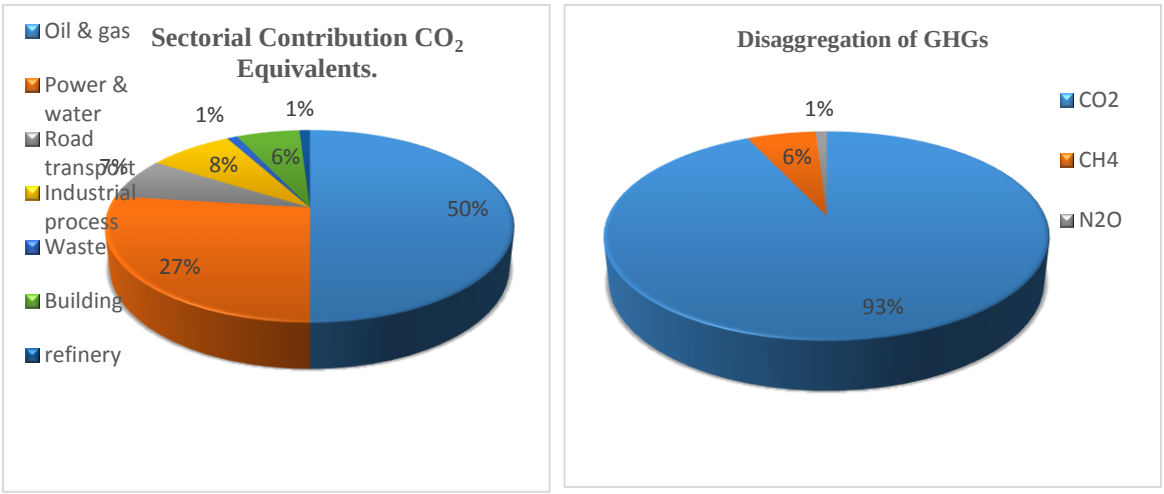

Figure 2.2: GHGs inventory in Qatar: Sectorial Contribution CO_2 Equivalents and Disaggregation

For Qatar alone the removal of CO_2 from the raw natural gas from the Qatari North Fields amounts to an annual CO_2 emission of over Million ton per annum (MTA). This is based on a CO_2 fraction of 2% in the raw natural gas, and the current level of Liquefied Natural Gas (LNG) export of 77 MTA There is an additional, substantial amount of CO_2 produced during the liquefaction process; a considerable amount of energy is required to liquefy the gaseous methane at -161 ºC.

2.2 CO_2 mitigation technologies:

Enhancing the carbon capture and storage (CCS) overall efficiency will become progressively more vital in the near future, as the adaptation of several various CO_2 capture techniques from the flue gas are economically infeasible at the current time. On the other side, it is predictable that CO_2 will become available from several diverse sources. For the Gulf Cooperation Council (GCC) countries this will include refiners, petrochemical processes, power plants, LNG production facilities and gas separation at processing plants.

Various methods exist for CO_2 mitigation considering the impact of CO_2 as the main contributor to climate change (Hoyt, 1979) these include enhanced oil and gas recovery, CO_2 conversion to chemical feedstock and fuels (Laumb *et al.*, 2013). These methods are mostly focused on CO_2 utilization following capture. Figure 2.4 shows some common methods of CO_2 mitigation.

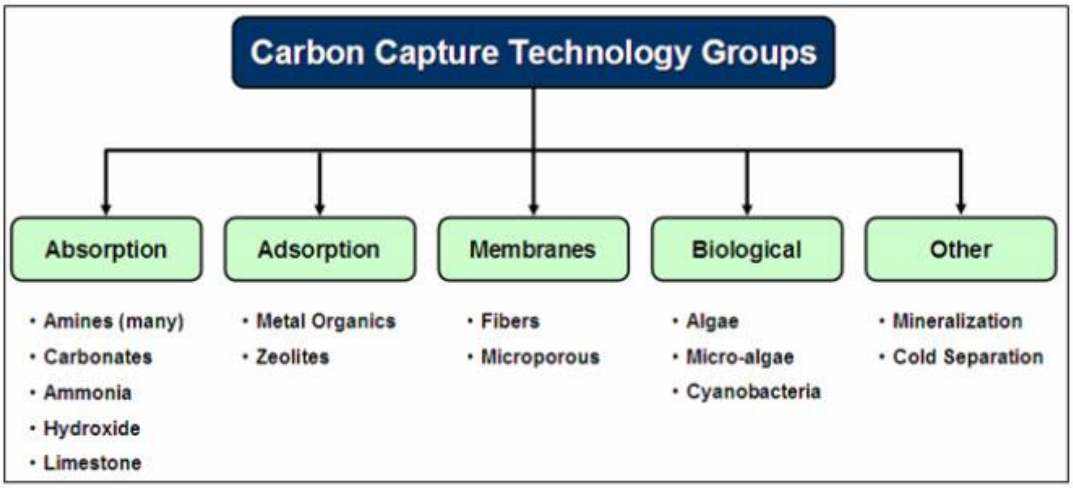

Figure 2.3 Carbon capture technologies (Institute, 2009)

At the current time processes based on chemical adsorption for CO_2 capture and storage have an estimated average cost 55US$/ton CO_2 (Finkenrath, 2011). The economic infeasibility comes from the regeneration step which contributes to around 75% of the energy consumption which is

directly related to the cost. For power plants with an efficiency of 35-45% the energy cost can be as high as 10% which increases the demand for more economically feasible and sustainable approaches to be considered in the CCS chain.

Biological conversion is the only method capable of direct CO_2 mitigation (Judd *et al.*, 2015). Utilization of captured CO_2 as feed for different processes, offers openings to counterweight the substantial high capital cost related to the capturing of CO_2. The potential for algae to utilize and capture CO_2 has other advantage over the alternative for CO_2 mitigation. CO_2 capture by algae is considered efficient and sustainable since the biological process requires only daylight, ambient temperatures and food source (CO_2) to be sustained. The key product of the biological process is considered to be the biomass which can be utilized to produce biofuel, such as biomethane, biodiesel and biohydrogen (Brennan e Owende, 2010) or other high-value products which include proteins and fatty acids (Borowitzka, 2013). The photo-bioreactor (PBR) technology e,g pond system has some attractive properties such as the reactor can be flexible in terms of CO_2 load and scalability, shock load resistance and low operational cost. The process is considered flexible since it can accommodate CO_2 from several sources and can be integrated with other processes such as wastewater treatment plants and power plants. In these processes CO_2 injected to biomass in most cases green algae leads to direct conversion of CO_2 to biomass in an engineered system such as photo-bioreactors. Biological process if compared with other CO_2 capture methods, such as chemical processes and oceanic fertilization would offer a more viable and sustainable solution for economic and environmental considerations.

The importance of algae has increased due to the fact that under different conditions, favorable or unfavorable, these species can grow and produce valuable by-products. The attractiveness of biological photo-bioreactors technology as a means of CO_2 capturing and reusing is

strengthened by the country's extremely high average number of daylight hours. At around 3700 hours, Doha experiences more than twice as many annual hours of sunshine than most European capital cities (London, Paris, and Stockholm, for example, each have 1800 hours or less). The light intensity provided during the Qatari summer is around 95,000 lux (Wilson *et al.*, 2012), or about 139 W/m^2, compared to less than half of this value in most EU countries and regions of North America. Since the consumption and fixation of CO_2 relies on illumination and benefits from higher intensities, the hours of sunlight specifically is a crucial factor in the process economics. For example, based on a study performed at MIT (MA, USA), over a seven day growth period microalgae have been shown to remove 82% of CO_2 on sunny days compared to 50% on rainy days (Vunjak-Novakovic *et al.*, 2005).

2.3 Microalgae species:

Microalgae belong to huge collection of organisms ranging from multicellular to unicellular species. Algal species can exist individually or in colonies in freshwater, wastewater and marine water (Butterfield, 2000). The size of microalgae range from 1 to 300 (μm). Like any other plants, microalgae perform the photosynthesis process which includes the use of solar photon captured from the sun and the available carbon source (e.g organic matter and CO_2) to grow and produce the atmospheric oxygen. The biodiversity of microalgae is enormous; it has been estimated that more 800,000 algae species exist while only 50,000 species are described (Keeling, 2004). The biochemical composition of microalgae varies depending on species themselves and on cultivation conditions. Microalgae culture can be altered or changed by changing the conditions of growing media, the most important factors that have direct effect on microalgae culture change and growth are temperature, light intensity, pH, organic source and nutrients.

Algae is simple in its structure because of the absence of organs that exist in other land plants (Znad *et al.*, 2012). All algae species are capable of performing the photosynthesis process and as a consequence they produce O_2 (Znad *et al.*, 2012). These species are classified into microalgae and macroalgae based on their size (Znad *et al.*, 2012). Statistical analysis of the work that has been done on CO_2 mitigation by algae showed that Chlorella vulgaris is the most popular due to its robust characteristics.

Algae species are rich in oil content compared to any other crops such as corn or oil palm. Algae can produce higher oil yield with less farming land requirements as shown by Table 2.2. Based on the different compositions of each algae strain, algae can have a very wide range of tolerances

against CO_2 concentration as well as other conditions such as temperature and pH. Table 2.3 shows CO_2 tolerance of various algae species.

Table 2.2: Typical yield and land data (Sudhakar et al., 2011)

Crop	***Oil yield (gal/acre-yr)***	***Land area needed (million acre)***
Corn	18	2222
Cotton	35	1143
Soyabean	48	833
Canola	127	315
Jatropha	202	198
Oil palm	635	63
Microalgae (15% oil)	1200	33

Table 2.3: CO2 Tolerance of Various Algae Species(Goswami et al., 2012)

Species	**Known maximum CO_2 concentration**
Cyanidium caldanum	100%
Scenedesmus sp.	80%
Chlorococcum littorale	60%
Synechococcus elongatus	60%
Euglena gracilis	45%
Chlorella sp.	40%
Eudorina spp.	20%
Dunaliella tertiolecta	15%
Nannochloris sp.	15%
Chlamydomonas sp.	15%
Tetraselmis sp.	14%

Based on the typical molecular formula for algal biomass, the average CO_2 fixation rate is 1.88 times the biomass productivity (mg/ L. day) (Judd *et al.*, 2015). This means that for the production of 1 kg of algae around 1.8 to 1.9 kg of CO_2 is required. Clearly, there is a significant variation in the amount of CO_2 consumed, even for the same type of algae. Chlorella appears to be the algae species providing the highest rate of CO_2 consumption, at over 1 g per day per L (Ho *et al.*, 2011). An important design parameter is the growth rate of the algae itself, which will impact not only on the CO_2 demand but also depends on various operating conditions such as light intensity and temperature. Figure 2.4 shows CO_2 consumption rate for a range of algae strains.

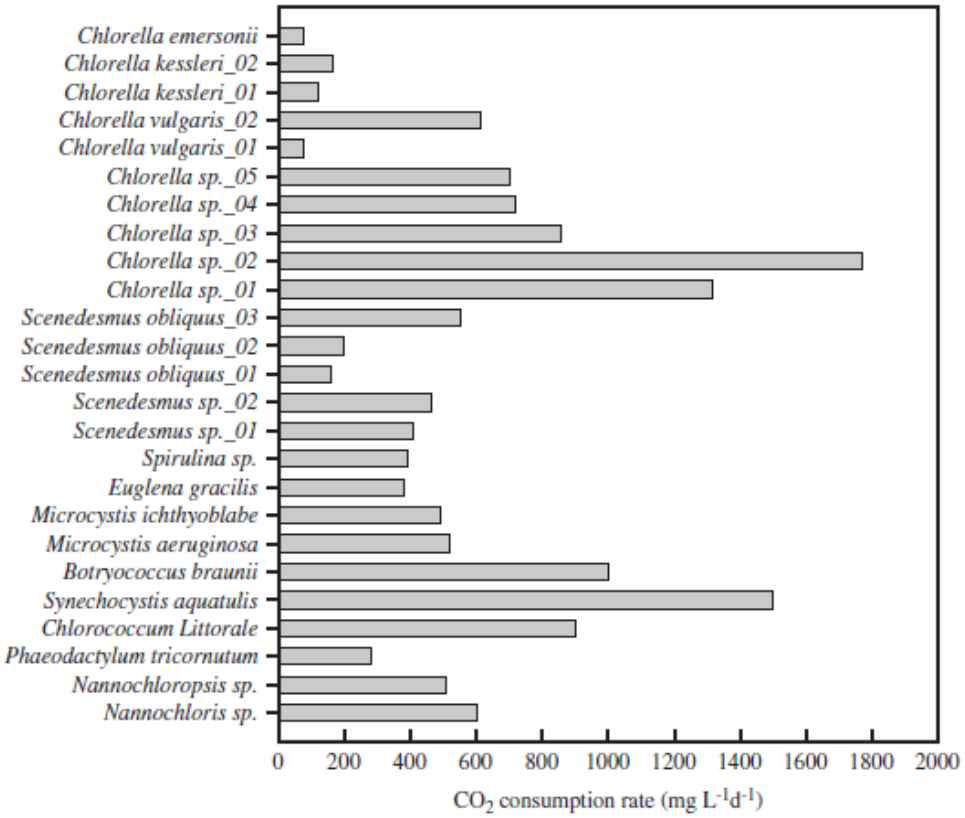

Figure 2.4: Overview of CO_2 consumption for a range of different algae, from (Ho *et al.*, 2011).

2.4 CO_2 Capture by Microalgae:

Different reactor configurations can be used for algae cultivation. The various reactor systems used for algae cultivation depends on several variables that will be discussed in section 2.7. In this section the focus will be on the reported data for CO_2 capture by green algae. Carbon dioxide uptake by the algal system depends primarily on algae growth rate (Chiang *et al.*, 2011). The water flow rate through the system showed to have a minimal effect of CO_2 utilization. As CO_2 uptake performance is dependent on the algae growth rate, there are certain requirements for the system such as the reactor capacity to allow appropriate CO_2 retention time. Studies performed on CO_2 uptake by microalgae were based on bench-scale single reactor of small volume (Tang *et al.*, 2011). The use of single reactor of a small volume results in small CO_2 percentage removal and thus low CO_2 uptake capacity. On the other hand, studies conducted on large scale systems which provide sufficient reactor volume to allow more CO_2 removal showed high CO_2 removal rate. Large scale systems include closed reactors (Li *et al.*, 2013), multi-stage reactors (Cheng *et al.*, 2013; Lam e Lee, 2013) or reactors with recycle flows (Lam e Lee, 2013). Table 2.4 summarize the CO_2 fixation reported by different studies in different types of reactors and different operational conditions

Table 2.4 : Summary of CO_2 fixation rate reported by different studies in different types of reactors and under different operational condition

system	*Gas flow (L/min)*	*Algae Species*	*CO_2 %*	*Cell Density (growth)*	*CO2 Fixation*	*Temp*	*Ph*	*References*
External loop airlift photobioreactor	-	-	-		-	25 C	8	(Pirouzi *et al.*, 2014)
Membrane-sparged helical tubular photobioreactor	2.7-4.5	Chlorella Vulgaris	0.045-0.093% mole fraction	0.75-0.95 g/L	0.15 g/L.hr	25 C	7.02-8.25	(Fan *et al.*, 2008)
Long Tubular Photobioreactor	0.15	NOA-113	15% (v/v)	2.5 g/L	3.5 g/day.reactor	25 C	4.5-6	(Yoshihara *et al.*, 1996)
Tubular photobioreactor		Phaeodactylum tricornutum		2.29-4.10		20-22		(Molina *et al.*, 2001)
Three-stage serial tubular photobioreactor	-	Spirulina sp. and Scenedesmus	6-12% (v/v)	1.9-3.5 g/L	45.61-53.29%(SP) 13.56-28.08%(S.ob)	30 C	7.0-11.7	(De Morais e Costa, 2007a)
Tubular photobioreactors	200 L/min	Scenedesmus almeriensis	3 L/min		85-93%	35 C	7.8	(Fernández *et al.*, 2012)
Batch photobioreactor	20-40 ml/min	Chlorella pyrenoidosa and Scenedesmus abundans	10%	2.5-4.9 mg/L.hr	0.036-0.096 mol/20hr	35-45	-	(Kargupta *et al.*, 2015)
Bubble-column photobioreactors in batch operation mode	0.4 vvm.	Scenedesmus obtusiusculus	5-10% (v/v)	3,370-5,700 g/m3	470-970 g/m3.day	30 C	7.5	(Toledo-Cervantes *et al.*, 2013)
Large scale open system	8 L/hr	Scenedesmus obliquus SA1	0.03- 35% (v/v)	1.39± 0.023 g/L	34.85 ± 0.20-97.65 ± 1.03 mg/L.day	25-26 C	7-8.	(Basu *et al.*, 2014)
Glass columns	300 mL/min	D. pumila-3Dp86E-1	0.035,20,100%	1.34 g/L	1.5–2.0 L CO2/day per L culture	-	9-10.5	(Solovchenko *et al.*, 2014)
5 column-type photobioreactor		Chlorella vulgaris	0.5%, 1%, 2% and 5%	0.5-0.8 g/L	63.1-162.4 mg/l/day	25–28 ◦C	4	(Lam e Lee, 2013)

2.5 Photo-bioreactor technologies:

There are two main types of photo-bioreactors used for algae growth, open and closed systems. Open photo-bioreactor systems such as waste stabilization pond systems (WSPs) and high rate algal ponds (HRAP) are normally open to atmosphere and exposed to the sun and environmental factor. In general, WPs are used for wastewater treatment which is considered as "green treatment". Effective wastewater treatment can be accomplished through integrated growth of microalgae and heterotrophic bacteria. Microalgae produces oxygen as a byproduct from the photosynthesis process. The produced oxygen is utilized by the heterotrophic bacteria to bio-oxidize the organic compounds in wastewater at aerobic conditions. The final product of the bio-oxidation process is carbon dioxide, which is consumed by microalgae in the photosynthesis process. HRAP consists of of algal reactor and strong oxidation ponds combined together. HRAP offers a much more effective wastewater treatment option compared to typical oxidation ponds. The high efficiency of the HRAP is primarily caused by strong microalgae photosynthesis resulting in more oxygen as byproduct to supply the aerobic oxidation process and consumption of wastewater nutrients by algae, which will be converted to biomass. Open photo-bioreactor systems are hard to control and it can be contaminated easily (Znad *et al.*, 2012). Closed systems include tubular, mechanically stirred, airlift and bubble column. Closed systems are easier to control and can achieve higher mass transfer rates. Table 2.5 summarize the differences between open and closed algae growth systems

Table 2.5 Advantages and disadvantages of open and closed algae growth systems (Sudhakar *et al.*, 2011)

Parameter	***Open pond***	***Closed photobioreactor***
Construction	Simple	More complicated-varies by design
Cost	Cheaper to construction and operation cost is cheaper	more expensive construction, operation
Water losses	High	Low
Typical biomass concentration	Low, 0.1-0.2 g/l	High: 2-8 g/l
Temperature control	Difficult	Easily controlled
Species control	Difficult	Simple
Contamination	High risk	Low risk
Light utilization	Poor	Very high
CO_2 losses to atmosphere	High	Almost none
Typical Growth rate(g/m2/day)	Low:10-25	Variable:1-500
Area requirement	Large	Small
Depth/diameter of water	0.3m	0.1m
Surface: volume ratio	~6	

2.5.1 Tubular photo-bioreactors

Tubular PBR consists of long helical or straight tubes configured in various geometries, Tubular PBR aims to maximize the use of light from the source. The growth medium can be circulated by injection of gas at an end of the tube, which contains certain concentration of CO_2 and is allowed to exist the system at the other end of the tube. Experimental work showed that large scale tubular PBR usually fails due to oxygen accumulation (Grima *et al.*, 2000).

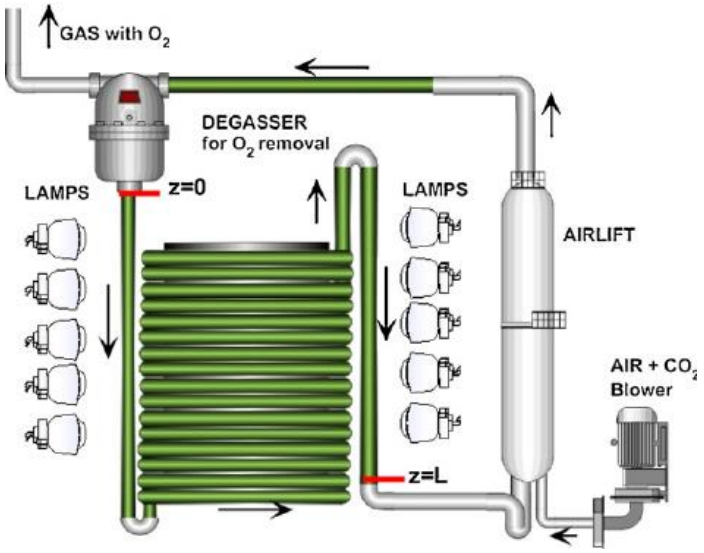

Figure 2.5 : Tubular photobioreactor diagram (Concas et al., 2010)

2.5.2 Mechanically stirred photo-bioreactors

Mechanically stirred PBR uses baffles to move the growth media, in order to achieve the transfer of air into the growth media. The stirred growth media can have some disadvantages such as high shear stress which causes damage to the wall of the cells(Grima *et al.*, 1996). On the other hand, if the growth medium is stirred slowly it will not expose all the cells to the light source and might limit the mass transfer.

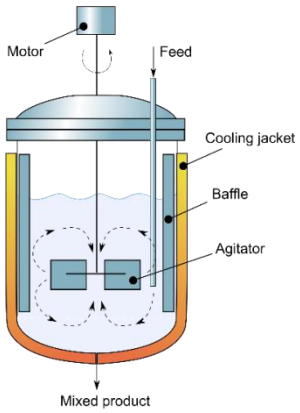

Figure 2.6: Mechanically stirred photo-bioreactors diagram (Pugliesi, 2009)

2.5.3 Airlift photo-bioreactors

Airlift PBR consists of a column separated into two sections, air/CO_2 is injected in one of the section sections which causes circulation of the growth medium. The injection section is called Riser and the other section is called Downcomer (Miron *et al.*, 2000).the Airlift PBR is mainly used for fermentation and wastewater treatment. The main difficulty with this type of PBR is small illumination area. Airlift PBRs showed good mass transfer, energy consumption and mixing.

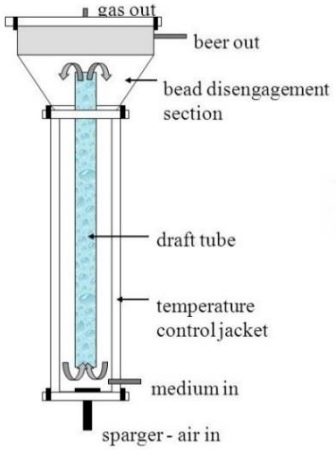

Figure 2.7: Airlift photo-bioreactors(Tyler, 2016)

2.5.4 Bubble column photo-bioreactors

Bubble column PBR consists of vertical cylindrical or rectangular column. The column is filled with growth medium, CO_2/air is injected at the bottom of the column by a sparging system. It is reported that. New version of the bubble column PBR can achieve efficient aeration and less pressure drop at high flowrates (Poulsen e Iversen, 1998).

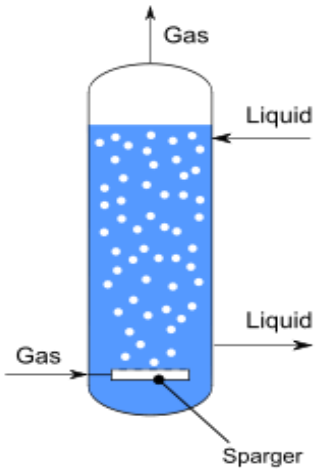

Figure 2.8: Bubble column photo-bioreactors diagram (Chanab, 2017)

Table 2.6 shows some of the advantages and disadvantage for some common types of PBRs adapted from (Ugwu *et al.*, 2008; Kunjapur e Eldridge, 2010; Panddey, 2014)

Table 2.6 Typical Advantages and Disadvantages of the Main types of PBRs (Ugwu et al., 2008)

Culture systems	**Prospects**	**Limitations**
Open ponds	• Relatively economical • easy to clean up after cultivation • good for mass cultivation of algae	• Little control of culture conditions • difficulty in growing algal cultures for long periods poor productivity • occupy large land mass • limited to few strains of algae cultures are easily contaminated
Vertical-column photo-bioreactors	• High mass transfer • good mixing with low shear stress • low energy consumption • high potentials for scalability • easy to sterilize, • readily tempered • good for immobilization of algae • reduced photo-inhibition and photo-oxidation	• Small illumination surface area • Their construction requires sophisticated materials shear stress to algal cultures • decrease of illumination surface area upon scale-up
Flat-plate photo-bioreactors	• Large illumination surface area • suitable for outdoor cultures • good for immobilization of algae • good light path • Good biomass productivities, relatively cheap • easy to clean up • Readily tempered • low oxygen build-up	• Scale-up require many compartments and support materials difficulty in controlling culture temperature some degree of wall growth • possibility of hydrodynamic stress to some algal strains
Tubular photo-bioreactors	• Large illumination surface area • suitable for outdoor cultures • Good biomass productivities relatively cheap	• Gradients of pH • Dissolved oxygen and carbon dioxide along the tubes • Fouling • Some degree of wall growth • requires large land space

The design of PBRs undergone different modification during the last decay in order to overcome some of the mentioned limitations. For example, to prevent oxygen accumulation in the system an automated oxygen degassing system was utilized. The length to flow velocity ratio was calibrated to achieve optimal algal growth rate. According to literature, the main failure of large-scale tubular photo-bioreactor is the high dissolved oxygen (DO) value (A Herzog, 1999). It was reported that the DO value in some of PBRs can reach as high as 20 mg/L, and can cause inhibition of algae growth (Stewart e Hessami, 2005). Researchers reported other issues with tubular photobioreactor such as limited scalability and difficulties in building and maintaining the system. Other researchers tried to eliminate excess oxygen by bubbling air/N_2 into the photo-bioreactor. These techniques can lower the free oxygen in the system, but the dissolved oxygen (DO) remains almost unaffected.

The influence of the overall reactor design represents the starting point in algal growth optimization. Various closed PBR configurations have been considered, ranging from flat plate reactors, air-lift reactors, bubble columns, and tubular reactors. Of the system facets impacting on algae growth, however, tolerance to changes in loading is of some practical significance since the CO_2 may be available from different sources and so delivered at various and varying flow rates and concentrations according to the origin of the flue gas stream. Different studies have evaluated the effect of the CO_2 concentration on the algae growth rate and confirmed that algae growth rate increase by increasing the concentration of CO_2 in aeration stream. The concentrations of CO2 in aeration stream was referred to to vol % or mol % CO_2 balanced by nitrogen.

2.6 Photo-bioreactor scale up challenges

Microalgae growth requires an appropriate amount of light energy to sustain microalgae growth rate. inadequate light source reduces the growth rate and excess light can cause photoinhibition and light saturation effect, i.e. more photons being absorbed than can be processed by the reaction centres; this excess energy is quickly lost, wasted as re-emitted as fluorescence or heat. In fact due to the large antenna size of the photosynthetic apparatus of microalgae, the algal cultures productivity under sunlight is at best only about 1/3 to 1/4 what might be anticipated from laboratory experiments at low light intensity. Over the last years, various solutions have been proposed to overcome limitation of light to the productivity of algae, of these;

- Mixing algal cultures rapidly so that all cells get their moment in the sun ('flashing light effect') (Benemann *et al.*, 2007).
- Dispersing sunlight through the culture by means of prisms or, more recently, optical fibres and LEDs (Benemann *et al.*, 2007; Yeh e Chung, 2009)
- Using vertical panels that do not receive full sunlight, as does a horizontal pond (Benemann *et al.*, 2007).
- Varying the illumination angle at the surface of the PBR (Morita *et al.*, 2000).
- Use Photo-bioreactors with static mixers to circulate the culture/cells between light and dark districts (Ugwu *et al.*, 2005).

Most of the Photo-bioreactors are suitable for small-scale cultivation, but are complex to scale up. The light source is considered one of the main challenge in the scale-up process. Several illumination strategies were developed to overcome the restriction of light and improve algae

growth rates (Chen *et al.*, 2011) such as, the use of reflecting sheets to transfer the light to the system (El-Shishtawy *et al.*, 1997) . Other researchers developed systems made of glass with artificial lighting [Lamps] fixed in photobioreactor (Tsygankov *et al.*, 1994). (Hsieh e Wu, 2009) developed an open system photo-bioreactor with transparent chambers for cultivation of algae under continuous light source by halogen lamps, providing a large area of illumination, improving light utilization of microalgae. Several different photo-bioreactors were designed to increase the effectiveness of microalgae growth, but they still face the limitation of high power consumption and cost due to the required artificial light source. To discover the full commercial potential of algae cultivation, highly efficient, durable and cheap source of light is required.

2.7 Reactor conditions optimization:

2.7.1 Temperature:

Temperature control is one of the most important factors to be considered in algal biomass production, each species of algae has an optimum growth temperature. High temperature accelerate the algae growth and low temperatures tend to inhibit the growth of algae(Znad *et al.*, 2012). Optimal temperatures can also be affected by other variables, such as the light intensity(Znad *et al.*, 2012).

2.7.2 pH:

The pH is very important since it affects nutrients solubility and availability, pH also effects substances transportation and the activity of enzymes. Most algae species favor neutral pH (Znad *et al.*, 2012). Some algae species tend to tolerate alkaline medium while other species can tolerate low pH values (Sankar *et al.*, 2011). There is a strong and complex relation between the pH value and CO_2 concentration, increasing the CO_2 concentration will lead to an increase in the algae growth, but at the same time the CO_2 will lower the pH value which might not be favorable by the algae strain(Znad *et al.*, 2012).

2.7.3 Light intensity:

Light is considered to be the elementary energy source for algae. Light intensity is a very important factors for an algae culture to success (Wong, 2012). Light intensity must be controlled and monitored. It's important that the light intensity is strong enough to penetrate the algal culture and reach all cells but not too strong to the point where it will stress the algae (Pandey *et al.*, 2011). Table 2.7 shows the effect of light intensity on the production of biomass and CO_2 fixation.

Table 2.7: Reported CO2 fixation rates and bimass growth at diffierent light intensities, Anabaena sp (Judd et al., 2015)

Light intensity, µmol m^{-2} s^{-1}	***CO_2 fixn. Rate, g $L^{-1}d^{-1}$***	***HRT, d***	***Max. biomass concn, g L^{-1}***	***Inlet CO_2 %v/v***	***Flow rate vvm***	***g CO_2 g $biomass^{-1}$ d^{-1}***
900	1.45	2-3	3	0.03*	0.2	0.48
0-100†	0.43	3.3	0.76	10.6	~3 x 10^{-4}	~1
250	0.65-0.8	5	0.58-1.2	5-15, 10	0.04	0.67-1.12
650	0.16-0.58	0.7-6	0.35-0.95	0.03*	0.13-0.75	0.17-1.7
975	0.25-0.65	0.7-6	0.45-1.35	0.03*	0.13-0.75	0.18-1.44
1625	0.36-1	0.7-6	0.5-2	0.03*	0.13-0.75	0.18-2

2.7.4 Mixing:

In order for the photobioreactor to perform effetely, mixing rate must be considered as an important factor. Usually low mixing rates can prevent proper gas transfer and allow the culture to settle which will cause the algae to be less productive. On the other hand, high mixing rates can cause shear to the cells which will lead to the culture death. Some of the common methods to mix the cultures of algae are pumping and mechanical mixing (Znad *et al.*, 2012).

2.7.5 CO_2 and O_2:

Microalgae has a better CO_2 biological fixation compared to other plants (Znad *et al.*, 2012). microalgae species has different tolerances towards CO_2 concentrations. Gaseous concentration of CO_2 does not reflect the concertation that the algae is exposed in the liquid suspension due to mass transfer resistance, resulting from CO_2 concentration and pH gradient (Znad *et al.*, 2012). Low CO_2 concentration such as the atmospheric concentration [0.033%] can limit the growth of algae due to fact that roughly 50% of the algal biomass is composed of carbon (Wong, 2012). Microalgae need to have a high CO_2 sequestration capacity and the ability to live under high CO_2 concentrations (Wong, 2012). Oxygen is also very important for the growth of algae which is

often related to the CO_2 transfer rate, if O_2 concentration levels increase above the saturation it can lead to inhibition of photosynthesis process in the algal culture due to photo oxidative damage. The accumulation of O_2 can be avoided by using a degasser to allow the produced O_2 to be released (Znad *et al.*, 2012).

2.7.6 Nutrients:

Nitrogen is the second most important nutrient for algae growth following carbon (Becker, 1994). Nitrogen is associated with primary metabolism of microalgae due to its role in building proteins and nucleic acid (Green e Durnford, 1996). Algae culture tends to have lower growth rates and productivity under low nitrogen content (Znad *et al.*, 2012). N-starvation can lead to more lipid production at the expense of other components such as proteins (Wong, 2012). The third most important nutrient for algae growth is Phosphorus. Phosphorus should be added in excess due to the fact that not all phosphorus is bioavailable (Znad *et al.*, 2012). Other metal traces and vitamins are also required for effective cultivation, such as (Cu, Mg, Zn and B12 vitamin) (Becker, 1994; Utex, 2014).

2.7.7 Gas transfer/Mass transfer:

Gases introduced into a photo-bioreactor serve multiple proposes including: carbon supply [CO_2], mixing, increase light exposure for high density cultures, pH control and removing excess O_2 (Znad *et al.*, 2012). All algae cultures use inorganic carbon that can be supplied to the system in multiple chemical forms such as CO_2(aq), CO_3^{2-} , HCO_3^-, H_2CO_3 as shown in Figure 2.10. These variable chemical forms can be controlled by temperature and pH (Carvalho *et al.*, 2006). The use of any of the mentioned chemical forms compared to the other is not important because of the fast chemical reaction that interconverts between them (Joel C. Goldman e Riley, 1981).

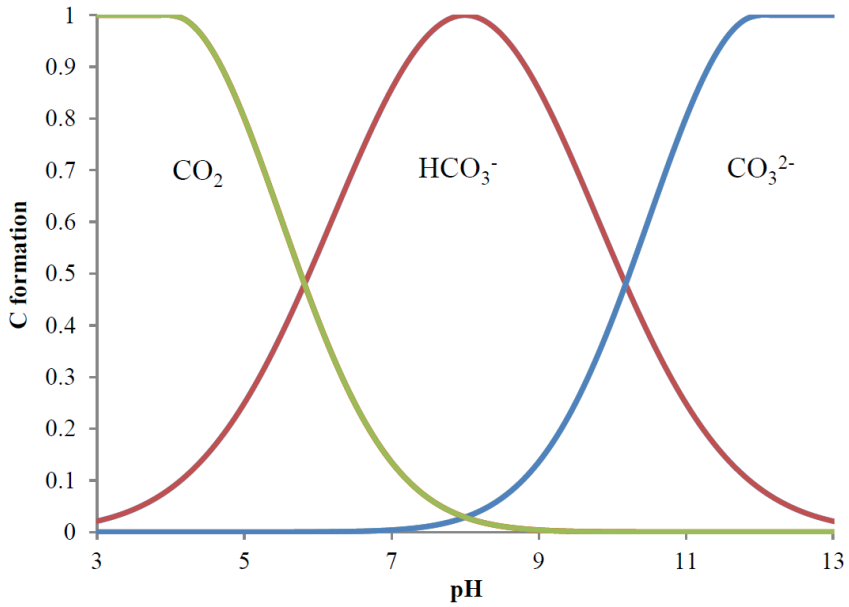

Figure 2.9: chemical forms of inorganic carbon (Abdulsada, 2014)

When CO_2 is introduced to the photo-bioreactor a concentration gradient forms as CO_2 is consumed by algae cells or lost to the atmosphere (Carvalho *et al.*, 2006). Taking in consideration that the gas/liquid mass-transfer resistance and the overall mass-transfer resistances are very close in magnitude, the mass transfer rate of CO_2 is mostly controlled by the liquid film (Carvalho *et al.*, 2006). Recent studies showed that the mass transfer coefficient

(kl_a) is highly dependent on the process dynamic (Fan *et al.*, 2008). Table 2.8 shows the reported mass transfer values for several PBR systems.

Table 2.8: Reported mass transfer values for PBR (Judd et al., 2015).

Reactor configuration	*kLa, h^{-1}*
External loop airlift	17-24
Membrane-sparged tubular reactor	250-430
Coarse bubble sparged reactor	20-65
Membrane contactor reactor	2.5-30
Tube	18
Column	up to 23
Raceway pond	up to 9.6

2.8 Nutrients removal & wastewater treatment:

Wastewater treatment has three main processes; physical, chemical and biological. Physical processes include screening, filtration and sedimentation. Chemical processes use chemical reactions to remove contaminants, usually by precipitation. Biological processes utilize organisms to degrade and remove organic matter from wastewater.

Although conventional treatment processes successfully remove organic matter and suspended solids from wastewater, the removals of nutrient in these processes are limited. Microalgae gained a lot of attraction due to their important role in uptake of nutrients/pollutants from wastewater and their ability to capture CO_2 and produce biomass at the same time. The basic role of microalgae in nutrient removal is explained by William Oswald shown in Figure 2.11:

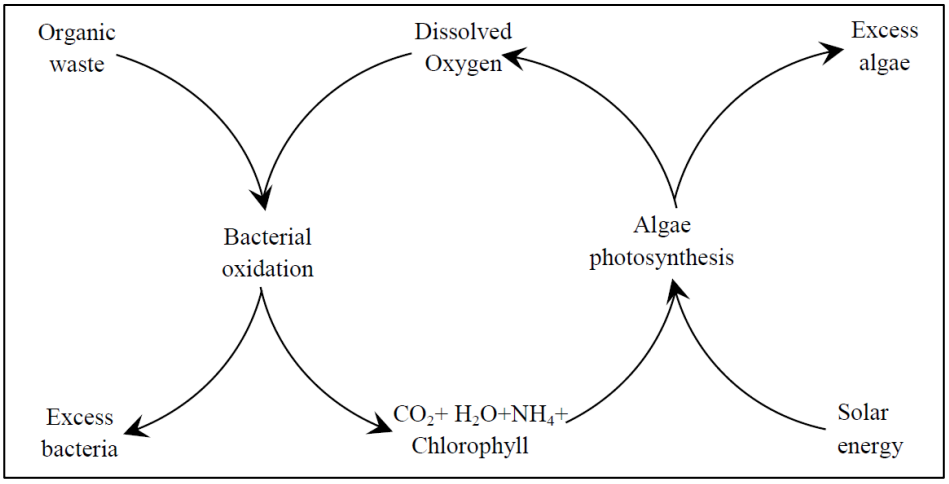

Figure 2.10: basic role of microalgae in nutrient removal (Abdulsada, 2014)

During the photosynthetic process algae uses CO_2 as carbon source and nitrogen and phosphorus for the cellular function. Which results in nutrients removal as well as CO_2 capture. Oxygen (O_2) is also produced as a by-product which can be used to biodegrade organic pollutants (Abdulsada,

2014). Microalgae can assimilate nitrogen and phosphorus from wastewater and reduce their concentration in wastewater via various methods which include the following:

- Direct mechanism through the diffusion of nutrients to the cell wall, which can be affected the surrounding water layer.
- Indirect Phosphorus precipitation as a result of high pH levels
- Indirect Ammonia stripping as a result of high pH levels

The use of Algae to recover nutrient – and specifically phosphorus – from municipal wastewater streams, offers the potential for prospective integration with wastewater treatment (Li *et al.*, 2011; Abdel-Raouf *et al.*, 2012), since microalgae can utilize low-quality water both as a source of water for the growth medium and nitrogen (N), phosphorus (P) and minor nutrients for algal growth. Algal cultures can resolve both economic and environmental challenges associated with conventional treatment methods while at the same time produce biofuels or other beneficial chemicals (Sivakumar *et al.*, 2012).

The effective growth of algae in wastewater rest on water quality determinants which include pH and concentration of nutrients (including N, P and organic carbon) as well as the availability of light, O_2 and CO_2. These variables will clearly depend on the WW source, as well as the algae species itself (Pittman *et al.*, 2011). Whilst many studies have focused on the influence of wastewater source (artificial, municipal, agricultural, or industrial wastewater) on nutrient removal and microalgae growth rates and/or biofuel production (Li *et al.*, 2011; Sturm e Lamer, 2011; Abdel-Raouf *et al.*, 2012), none thus far appear to have considered the influence of wastewater quality on the CO_2 uptake.

Algal-bacterial ponds or high rate oxidation pond was proposed for efficient removal of organic matter and nutrients (nitrogen and phosphorus) from wastewater. This treatment process considers as complete treatment alternative that has the ability to remove organic substances and nutrients with reasonable retention time and low operational cost. The basic model describing the algal-bacterial interaction in wastewater treatment pond was described by (Oswald *et al.*, 1953). The model shows the interaction between aerobic bacteria that consume carbon and oxygen to produce organic by-product, CO_2 and soluble nutrients, with microalgae which can use these by-products (organic, CO_2 and nutrients) in addition to the energy provided from the sun in the photosynthesis process to release O_2 and none harmful by-product.

Different studies have used algal-bacterial interaction for treatment of different types of wastewater. Most recently, (Zhu *et al.*, 2013) reported a removal efficiency of 65-76% of chemical oxygen demand (COD), 68-81% of total nitrogen (TN) and 90-100% of total phosphorous (TP) from piggery wastewater by fresh water microalgae Chlorella zofingiensis.(Wang *et al.*, 2010) reported COD removal of 50.9%, 56.5% and 83 % from primary influent of WWTP, primary effluent and centrate, respectively by green algae *Chlorella sp.* The study showed significant nutrient removals efficiencies: total nitrogen removals efficiencies were found to be 68.4%, 68.5%, 50.8%, and 82.8% in primary influent, primary effluent, secondary effluent, and centrate respectively. The same study reported a phosphorus removals of 83.2%, 90.6%,4.69% and 85.6 % in the same wastewater samples, respectively. (Aslan e Kapdan, 2006) found that microalgae Chlorella vulgaris is more effective in removing nitrogen compounds (72%) compared to phosphorus (28%) from synthetic wastewater. (Zimmo *et al.*, 2004) used a pilot-scale alga-based ponds (ABPs) to study nitrogen removal from domestic wastewater at cold temperatures (6.5 and 12.7 °C), warm temperatures (18.4 and

21.3°C) and high-low organic loading rates. Results showed higher overall nitrogen removal rate at warm temperature, but similar removals during high and low organic loading rates. (Tarlan *et al.*, 2002) showed that up to 58% of COD and 84% of water color can be removed from wastewater generated from pulp and paper industry using mixed algal culture.

Chapter 3: : Materials and methods

3.1 Algae Strain:

Pure microalgae strain (Spirulina platensis) was used in this study. Spirulina platensis (UTEX LB 2340) was purchased from UTEX Culture Collection of Algae, University of Texas at Austin, USA. Spirulina platensis (SP.PL) is characterized by its high robust characteristics and the ability of this strain to live in any aqueous media without the need for sterilization . The stock solution of this algae strain was maintained in liquid media for further use.

3.2 Growth media:

The medium used to grow Spirulina platensis was prepared by mixing the following chemicals per liter of solution: 16.8 g $NaHCO_3$, 2.5 g $NaNO_3$, 0.5 g K_2HPO_4, 1 g K_2SO_4, 1 g NaCL, 0.2 g $MgSO_4.7H_2O$, 0.04 g $CaCl_2.2H_2O$, 0.01 g $FeSO_4.7H_2O$ and 0.08 g EDTA. The pH of this media was found to be 9.5±0.2. The pH of the growth media was changed when required using 1 M NaOH solution or 1 N HCL.

3.3 Synthetic wastewater:

The synthetic wastewater was prepared to be similar the secondary effluent in Qatar. The synthetic wastewater was prepared by mixing the following chemicals per liter of solution: 2080 mg $(NH_4)_2SO_4$, 5720 mg $NaHCO_3$, 100 mg $FeSO_4 \cdot 7H_2O$, 1600 mg KH_2PO_4, 580 mg $CaCl_2 \cdot 2H_2O$, 1420 mg $MgSO_4 \cdot 7H_2O$, 2 mg $MnCl_2 \bullet 4H_2O$, 1 mg $Na_2MoO_4 \bullet 2H_2O$, 0.2 mg $CuSO_4 \bullet 5H_2O$ mg and 1 mg $ZnSO_4 \bullet 7H_2O$. The characteristics of the synthetic wastewater is summarized in Table *3.1*

Table 3.1: Characteristics of synthetic wastewater

Parameter	***Value***
COD (mg/L)	65
NH^{+}_{4} (mg-N/L)	22
NO_3	0.05
NO_2	0.1
Phosphorous	37

3.4 Algae Stock cultivation

Spirulina platensis (SP.PL) stock cultivation was carried out in 10 L flasks. Algal growth was started by inoculation a specific amount of algae with an initial optical density measured at 680nm of 0.1±0.03 AU. An air pump was used to supply the culture with the required aeration, Pumps were used to provide mixing. No CO_2 was added to the culture except for the diffused CO_2 from atmosphere. Lighting is provided by white florescent lamps, and the culture was maintained at a temperature of 24 ± 2 ˚C. Every 20 days the culture is provided with 1 L growth medium to maintain the growth. Once the culture reaches an optical density of 1.5 A.U it was considered ready for the experiment.

3.5 Analytical Methods

3.5.1 Algae growth rate and productivity:

The growth rate of SP.PL was followed by two main indicators; (1) optical density and (2) dry cell weight. The growth rate of spirulina platensis was followed up by measuring the optical density (OD) of algae samples every two days. The OD was measured at 680 nm and the blank sample used for the rest the spectrophotometer was the growth medium. The growth rate was calculated using equation (1):

$$Growth\ rate = \frac{\ln(OD_{680nm,t}) - \ln(OD_{680nm,0})}{\Delta t} \quad (1)$$

Where $OD_{680nm,0}$: initial optical density, $OD_{680nm,t}$: optical density on a selected day and Δt : The difference in time

The dry cell weight was determined using a pre-calibrated curve. The calibration curve was obtained by measuring the optical density of different algae stock solutions at 680 nm. Then, a 100 mL of algae solution was filtrated using 0.45 µm fiber glass filter, and the dry cell weigh collected on dried filter was determined. Drying was carried out inin an oven at 105 ◦C for 8 hrs. After that that the dry cell weight was correlated at 95 % confidence level to the measured OD as shown in Figure 3.1.

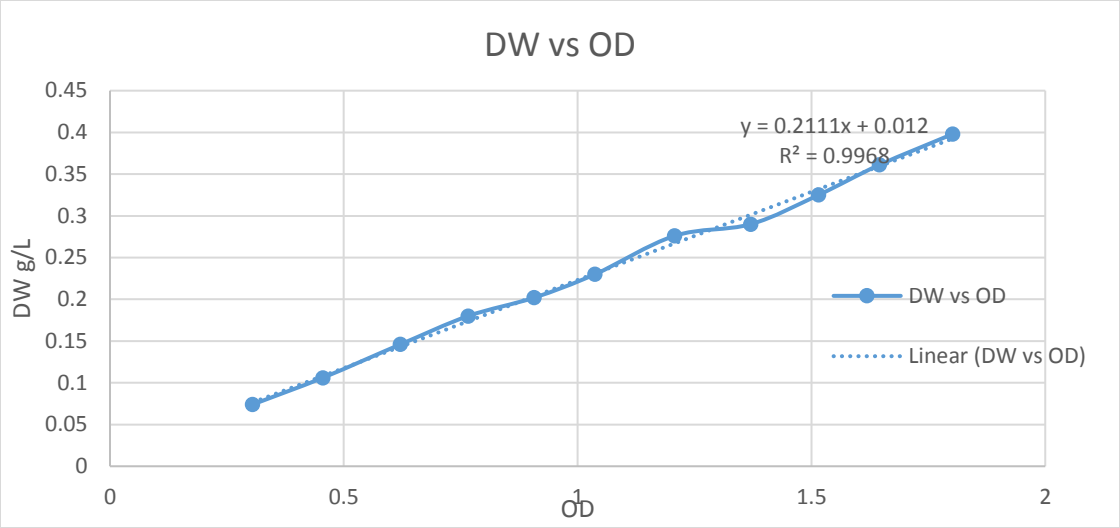

Figure 3.1 : The relationship between the measured OD and algae dry cell weight

The values of optical density and dry weight were used later to calculate biomass productivity and specific growth rate according the equation (2) and (3):

$$\text{Biomass productivity } (\text{g.L}^{-1}.\text{d}^{-1}) = \frac{(W2 - W1)}{\Delta t} \quad (2)$$

$$\text{Specific growth rate } (\text{d}^{-1}) = \frac{(\ln W2 - \ln W1)}{\Delta t} \quad (3)$$

Where W1: initial dry weight, W2: dry weight on a selected day and Δt: The difference in time

3.6 Chemical analysis:

- Total Solids (TS): Total solids were measured by drying 20 ml of the sample in an oven at 105 ◦C for 8 hours using pre-weighted crucible
- Total Suspended Solids (TSS): Total suspended solids were calculated by drying 20 ml of the sample using pre-weighted filters
- Dissolved oxygen (DO): Dissolved oxygen was measured using Orion 5 star® (Thermo scientific®) portable dissolved oxygen meter.
- pH: pH was measured using Orion 5 star® (Thermo scientific®) portable pH meter.
- Conductivity (EC): conductivity was measured using Orion 5 star® (Thermo scientific®) portable EC meter
- Chemical Oxygen Demand (COD): Soluble chemical oxygen demand tests (COD) were carried out using HACH COD reagents following the Standard Methods (APHA 1995), Method 5220D
- NH_4: ammonia NH4-N was measured according to Standard Methods, Method 4500–NH3 B and C (APHA 1995) using a HACH spectrophotometer at 425 nm (DR2700 HACH, CO, USA)
- NO_2^{-2}: Nitrite was measured according to the diazotization method using HACH powder pillows (Nitrite Method 8507) and HACH spectrophotometer at 505 nm.
- NO_3^{-1}: Nitrate was measured using HACH cadmium reduction method using HACH powder pillows (Nitrate Method 10020) and HACH spectrophotometer at 500 nm
- Total Phosphorus (TP): Total dissolved phosphorus was measured using HACH Molybdovanadate Method with Acid Persulfate Digestion (Method #10127)

3.7 Experimental work on carbon dioxide capturing

3.7.1 Experimental Set up

The potential use and the capacity of SP.PL green microalgae in capturing carbon dioxide were tested in lab-scale and pilot plant photo-bio-reactors (PBRs).

3.7.1.1 Lab-Scale set up

The capacity of SP.PL green algae as a CO_2 capturing technology was tested in batch lab-scale PBRs. A total of 6 PBRs 2 Liters each were used in this set of experiments. The PBRs were placed inside an incubator under controlled temperatures and continuous lighting. Figure 3.2 shows a schematic diagram for the CO_2 capture and nutrients removal under lab-scale experiments.

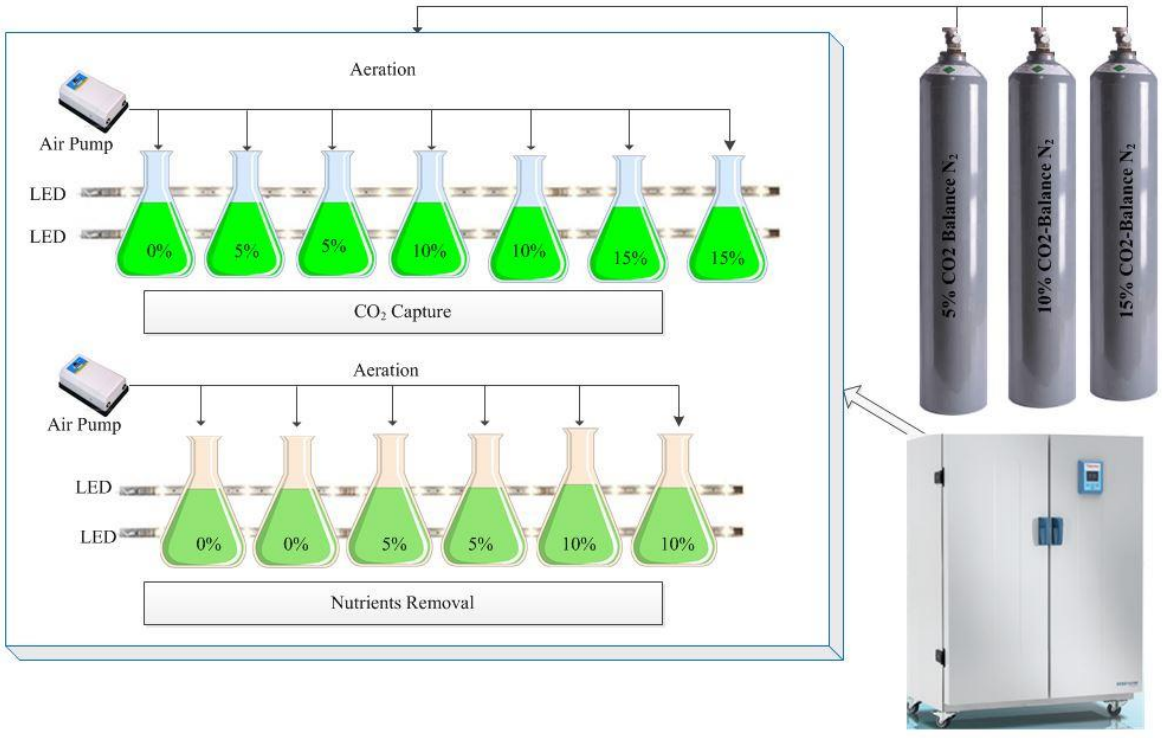

Figure 3.2: Lab-Scale PBRs setup

Batch experiments were carried out at 20, 25 or 30 ˚C. Lighting was provided to the PBRs via 6 white LED strips. The distribution of LED inside the incubator was adjusted to ensure sufficient and equal light distribution for all PBRs. Mixing of the reactor/culture was achieved by aeration via air pumps and CO_2 injection. The concentration of CO_2 used in these experiments were 5%, 10% and 15% balanced with nitrogen. Figure 3.3 shows the lab-scale setup for CO_2 capture under operation during the experiment.

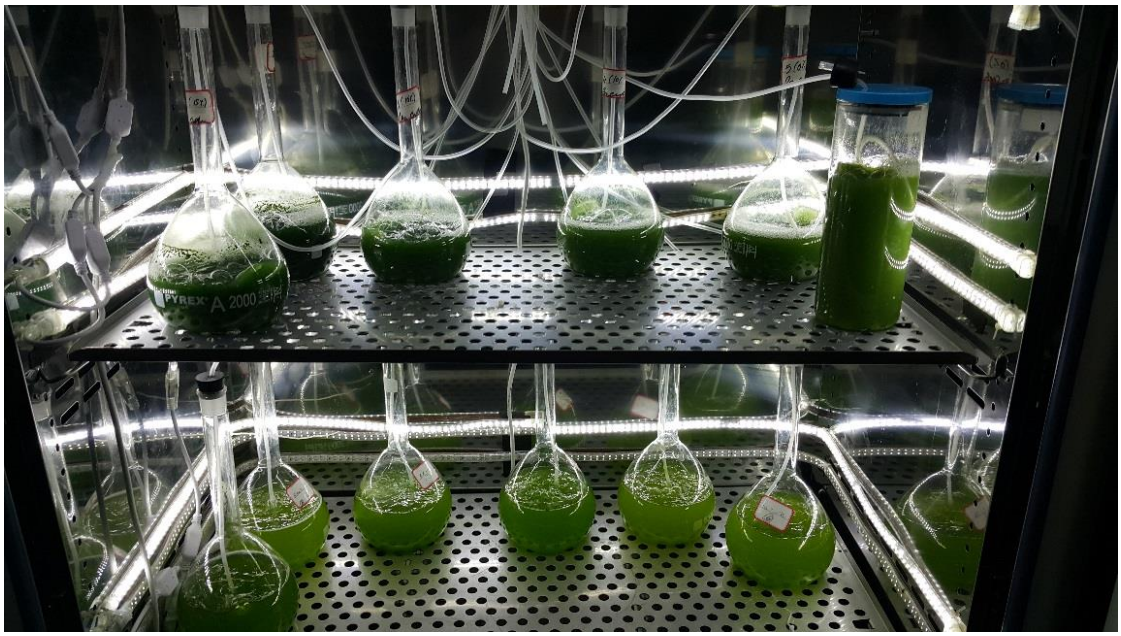

Figure 3.3: Lab-scale PBRs under operation

3.7.1.2 Pilot-Plant PBR

Pilot Plant experiment was carried out using a Greenline photo-bioreator as shown in Figure 3.4. The pilot plant equipped with (1) eight ports for CO_2 injection, (2) eight sampling points,(3) eight valves for oxygen release, (4) A row of 8 transparent and vertical tubes that enable algal culture utilizing the natural solar radiation in the growth process.

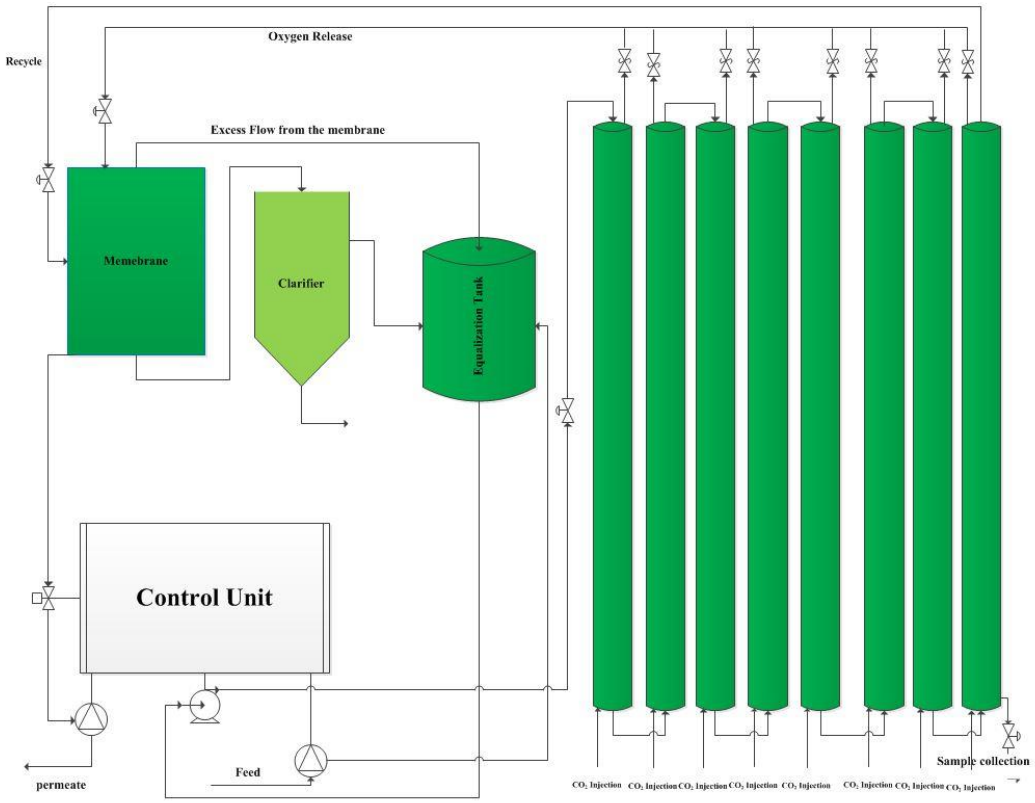

Figure 3.4: Pilot Plant process flow diagram

The tubes are arranged in rows and connected by collectors at the top and bottom. Transparent tubes are made of high-grade PET (Poly Ethyl Terephthalate). PET plastic is proved to be resistant to long-term exposure to UV radiation and resisting pH variation and has high solar irradiation transmittance. The system tubes are connected in series to accomplish: i) the essential

efficiency for each microalgae strain growing and the corresponding effect; ii) to maximize light reception, while maintaining small footprint, 2) feed pump to supply growth medium/wastewater, 3) a recirculation pump. The goal of the recycling pump is to achieve better mixing for algae, 4) water quality parameters sensors, the setup is equipped with light sensors, pH meter, temperature and dissolved oxygen electrodes that can be used to control wide water quality parameters of the treated wastewater, 5) mixing tank that can be used to mix the return water with fresh wastewater feed, and 6) clarification tank to recover microalgae. The hydrodynamic of the wastewater inside the pilot plant involving the integration of vertical path, turbulent flow, and low wastewater hydraulic retention can be effectively used to grow microalgae, at a high rate and efficiency. The system can be operated as a batch or continuous based on the configuration of the feed pump. Figure 3.5 shows the pilot plant during experimental testing.

Figure 3.5: Pilot Plant PBR under operation

3.8 Experimental procedures:

3.8.1 Lab-scale procedure

Lab-scale experiments were conducted using fresh water green algae SP. PL. during experiment the growth rates of SP.PL under different temperatures and CO_2 concentrations were followed. Initially, 800 mL of growth media was mixed 1200 mL of deionized water inside the photo-bioreactor. Then, all the photo-bioreactors were inoculated with SP.PL to produce a solution with an initial OD of 0.3 A.U. The incubator temperature was controlled at a temperature of 20, 25 or 30 ◦C. The photo-bioreactor was continuously mixed using air pumps (bubbling) which offers good mass-transfer and efficient mixing. The growth rate of SP.PL cultures was observed for 30 days and the culture growth was estimated by three analytical methods; (1) Total suspended solid (TSS), (2) Total solids (TS) and (3) optical density at 680 nm. The effect of CO_2 was inspected by injecting different concentrations of CO_2 (5%, 10% and 15%) on daily basis for 5 minutes.

3.8.2 Pilot plant procedure

The experiment is conducted to observe the growth of Spirulina platensis on large scale under different temperatures and CO_2 concentrations. As mentioned in the experimental setup the total capacity of the system is 250 L. Initially, 15 L of algae was add ed to 30 L of the growth medium to start algal inoculation. The pilot plant was s provided with 7.5 L of growth medium every two day to maintain the algae growth in the exponential phase CO_2 was injected to the system via injection ports every day. The amount of CO_2 was calibrated to give a concentration value of 5 and 10 v/v%. Samples were collected from the system to measure the growth rate, OD, conductivity, DO, pH, temperature and CO_2 consumption by SP.PL. Each Experimental run lasted for 42 days.

3.9 Experimental Work on Nutrient Removals

3.9.1 Experimental Setup and procedure:

The experimental set up used to study the performance of SP.PL green algae in removing nutrient from wastewater was the same as the lab-scale set up described in section 3.7.1.1. The procedure followed in this set of batch experiments was as follow: SP.PL was inoculated in the synthetic wastewater that contains specific concentration of nutrient (ammonia and phosphorous) under different temperatures and CO_2 concentrations. The growth rate of SP.PL and the % nutrient removals were monitored for 21 days. The initial nutrient concentration in all photo-bioreactors were the same. Mixing of the culture was achieved by aeration via air pumps. Wastewater samples were withdrawn from the photo-bioreactors and measured for optical density, NH_4-N, NO_2-N, NO_3-N, dissolved total phosphorus, dissolved oxygen, soluble chemical oxygen demand (CODs), and pH on daily basis. Each test was performed in duplicate and reported as an average value.

Chapter 4: : Results and discussion

4.1 CO_2 Capture in Lab-Scale PBR:

The objective of this part was to study the capacity of using SP.PL as a CO_2 capturing technology. Experiments were carried out at different temperatures (20, 25 and 30C) under a daily CO_2 injection dose of 0 v/v% (control), 5%, 10% and15%. Experiments were performed in duplicate and the average values were used in reporting the results.

4.1.1 CO_2 capture at 20 ˚C:

4.1.1.1 : Algae growth:

It is known that algae has the maximum absorbance in the wavelength range 600 to 690 nm, with a maximum absorbance around 680 nm. In this study, to explore the algae growth, the optical density was measured at 680nm (OD_{680}). Figure 4.1 shows the growth patterns of SP.PL (measured at OD_{680}) under different CO_2 dosage and at a temperature of 20˚C. Results are average of 2 replicate calculated at 95% confidence level

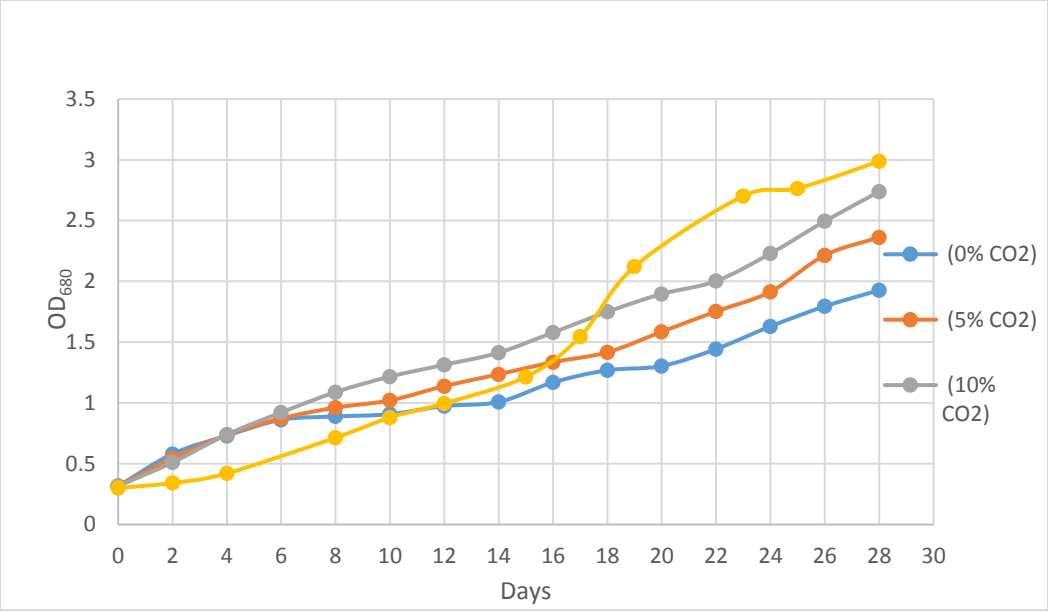

Figure 4.1: SP.PL growth under different CO_2 concentrations at 20 ◦C

It was noticed during these experiments that the growth patterns of SP.PL were characterized by very short lag phase (order of hours) and an extended exponential growth phase that starts directly after incubation. In addition, during the 28 days of incubation, stationary phase was not observed. The growth patterns of SP.PL during the first six days, under all experimental conditions, follow the exact same trend except for the sample injected with 15% CO_2. After the sixth day, samples started to show variation in the growth, and the sample injected with CO_2 dosage of 10% showed the highest growth, followed by sample injected with CO_2 dosage of 5% and 0%, respectively. However, it can be seen from Figure 4.1 that at later stage the growth pattern for the sample injected with CO_2 dosage of 15% improved and achieved the highest OD_{680} at the end of the incubation period. The maximum OD_{680} achieved by the end of the experiment were 1.93, 2.36, 2.738 and 2.99 for samples cultivated under CO_2 dose of 0, 5, 10, and 15%, respectively. The lack of lag phase for SP.PL under different CO_2 dosage suggesting that green algae has a good tolerance to different CO_2 levels. In addition, Figure 4.1 shows that

the growth of SP.PL at atmospheric CO_2 concentrations was slower than in the other studied conditions, suggesting that CO_2 at atmospheric concentration is not sufficient and there is a carbon limitation in this system. The trend observed for the algae culture injected with a CO_2 dosage of 15 % can be explain that at the beginning of incubation period the concentration was very low and the amount of inorganic carbon supplied to the system is greater than the CO_2 up take capacity of algae. However, after 10 days of incubation the algae was grown enough to balance the injected CO_2 to the system. Thus, the system follow the same trend as for other with a CO_2 dosage. Different trends were observed under the same range of CO_2 concentrations by other studies. (De Morais e Costa, 2007b) showed that the growth of SP.PL have increased until the CO_2 concentration of 5% (v/v), followed by a decrease observed for higher CO_2 concentrations (12% v/v). The same study showed that the growth rate of microalga Chlorella kessleri by increasing the CO_2 concentration in the aeration stream. The differences between this study and the previous studies can be due to differences in experimental set up and procedure

Figure 4.2 represents the summary of the average calculated growth rate of SP.PL under different CO_2 injection dosage at 20 ˚C. The growth rates were calculated using equation 1.

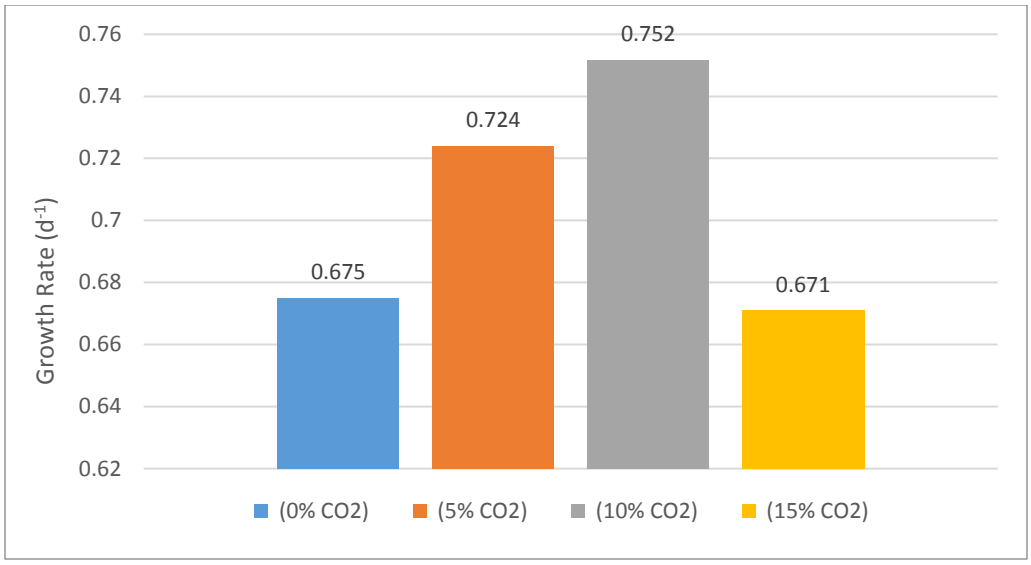

Figure 4.2: calculated growth rate under different CO_2 concentrations at 20 ºC

As the growth pattern of SP.PL in these experiments didn't show lag and stationary phases, the growth rates were calculated for the whole incubation period (from day 1 to 28). On other words, the time from day 1 to day 28 was assumed to be the exponential growth phase, the conditions that favors more CO_2 capturing. As it can be seen in Figure 4.2 the highest growth rate was reported for samples injected with a CO_2 dosage of 10%, followed by samples injected with a CO_2 dosage of 5%, 0% and 15%, respectively. The calculated growth rates were 0.752, 0.724, 0.675 and 0.671d^{-1} for samples injected with a CO_2 dosage of 10%, 5%, 0% and 15%, respectively. The lower Growth rate reported for the 15% sample despite achieving the highest OD_{680} is due to the delay in growth during the first 14 day as a results of inorganic carbon limitation. (Gonçalves *et al.*, 2014) reported a growth rate for Synechocystis salina in the range of 0.598 ± 0.012 to 1.65 ± 0.11 d^{-1} grown in CO_2 dosage in the range 10% to 5 % v/v. (De Morais e Costa, 2007b)reported growth rates for Spirulina sp. And Scenedesmus in the range 0.33 to 0.44 d^{-1} when these microalgae subjected to CO_2 concentrations in the range 0 to 12%. Lower specific growth rates were reported for S. obliquus (0.15 to 0.22 d^{-1}) and Chlorella

kessleri (0.20 – 0.27 d^{-1}) when grown with CO_2 concentrations in the range 0.04 to 18% (v/v). Later, (Chiu *et al.*, 2008) have shown that the specific growth rates for Chlorella sp. ranged from 0.127 to 0.492 when the cultures aerated with a gas stream containing 0.03 to 5% (v/v) of CO_2. It is worth the mention herein that the specific growth rates reported in this study are higher than the previous studies suggesting better ability for CO_2 capturing. The previous studies indicated that the observed decrease in specific growth rates for the cultures fed with higher concentration of CO_2 concentrations might be related to stresses in the photosynthetic characteristics of the selected microalgae and/or the low affinity of these algae to CO_2 (i.e. lower activity of carbonic anhydrase) (Yang e Gao, 2003; Xia e Gao, 2005). All these limitations were not observed in the present study. Moreover, as reported by different authors the initial concentration of green algae used in reactor inoculation plays an important role in the algae growth, it is not clear in all the previous study what was the initial concentration of algae used in each experiment.

The dry cell weight of SP.PL was used to calculate the biomass productivity using a predetermined factor (see equation 2). Figure 4.3 shows the biomass productivity for SP.PL under the same conditions reported in Figure 4.2

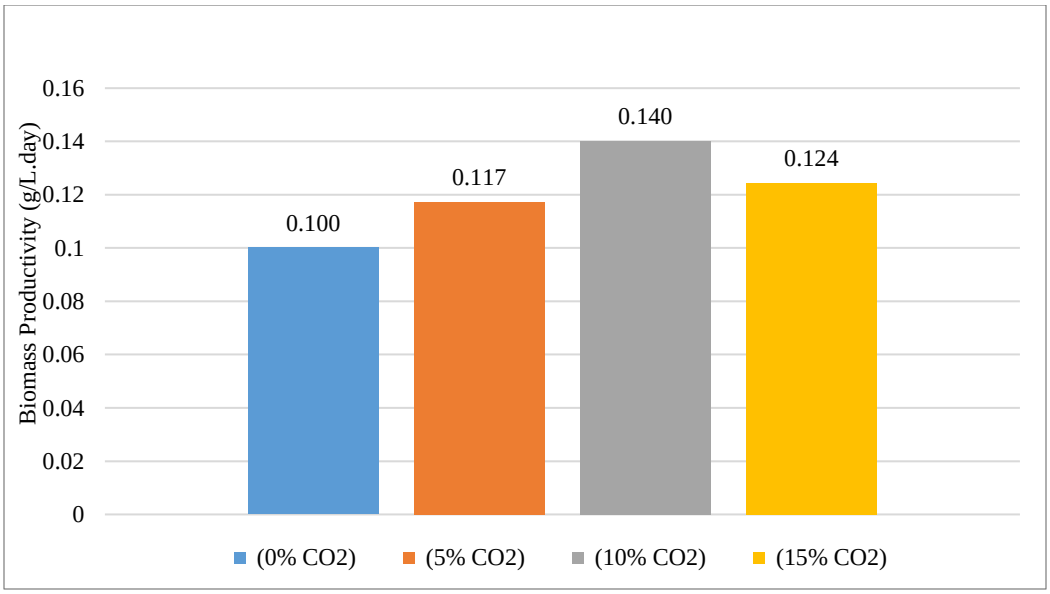

Figure 4.3: biomass productivity for different CO_2 concentration at 20C

it can be seen in Figure 4.3 that the there is a linear relationship between the biomass productivity and the injected amount of CO_2 except for the sample injected with 15% CO_2 which had some difficulties adapting to the higher CO_2 concertation due to the reasons explained in section 4.1.1.1. As the CO_2 dosage increase the biomass productivity increase. The reported biomass productivity range from 0.1 to 0.14 $gL^{-1}.day^{-1}$, and show a good agreement with the biomass productivity for similar species reported in literature by (Suryata *et al.*, 2010). (Walter *et al.*, 2011) reported biomass productivity values for SP.PL ranging from 0.015 to 0.03 $g.L^{-1}.day^{-1}$ under different light spectrum and no CO_2 injection, which indicate that CO_2 injection can lead to higher biomass productivity. (Shabani *et al.*, 2016) reported biomass productivities under different CO_2 concentration [0.03%, 2%, 5% and 10%] the reported productivities range was 0.065-0.09 $gL^{-1}day^{-1}$. The values reported by Shabani are noticply lower compared to the obtained results which can be due several reasons such as;mass transfer limitations, light intesnity, temperature and CO_2 difusion.

4.1.1.2 pH:

There is a strong relationship between the pH and the concentration of CO_2 in the water solution. It is known that increasing the CO_2 concentration in the water solution will lower the solution pH. However, if the up take capacity of CO_2 by the algae strain is balanced, the pH will be controlled and balanced (Znad *et al.*, 2012). Figure 4.4 shows the evolution of solutions pH during the CO_2 capturing experiments. Results are average of 2 replicate calculated at 95% confidence level. The pH of the solution was not controlled and left to evolve freely

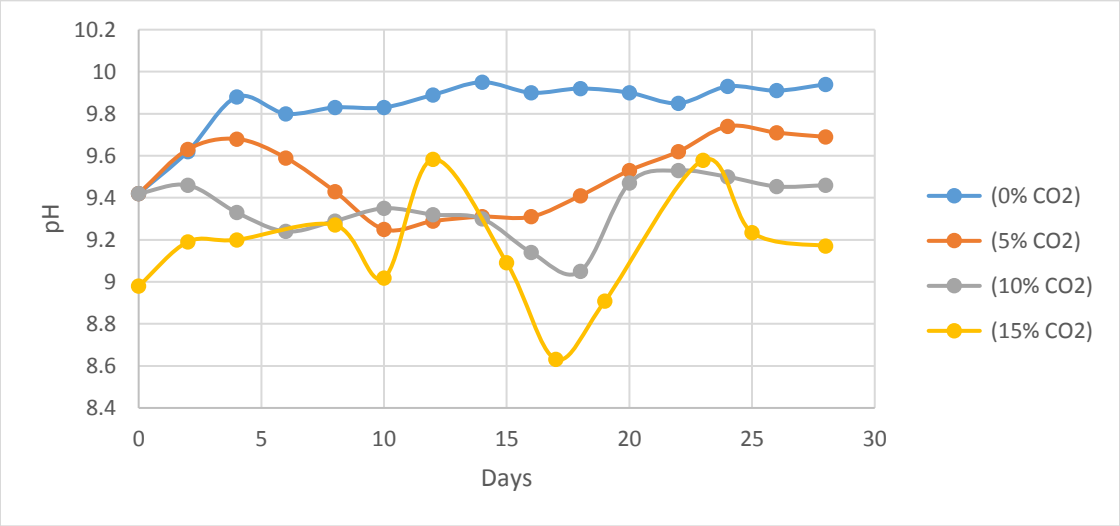

Figure 4.4: pH change during the experiment for different CO_2 dosage at 20C

Figure 4.4 shows that for control samples (0% CO_2 injection) the variation of pH is very small and not significant, the solution pH ranged from 9.42 to 9.94, with an average value of 9.8. The stable pH Evolution suggest that the amount of CO_2 in the solution is not a factor that affect the pH. All other samples injected with CO_2 dosage in the range 5%-15% showed a noticeable decrease in the solution pH. The average pH value for the culture decreased gradually from 9.51 to 9.15 for the samples injected with 5%, 10%, and 15% CO_2 as can be seen in Figure 4.5. as indicated before injected CO_2 is used as a carbon source for micro algae. In order for this carbon

source to be available for uptake by micro algae the gaseous CO_2 concentration should be increase to overcome mass transfer resistance and introduce to the solution (Znad *et al.*, 2012).

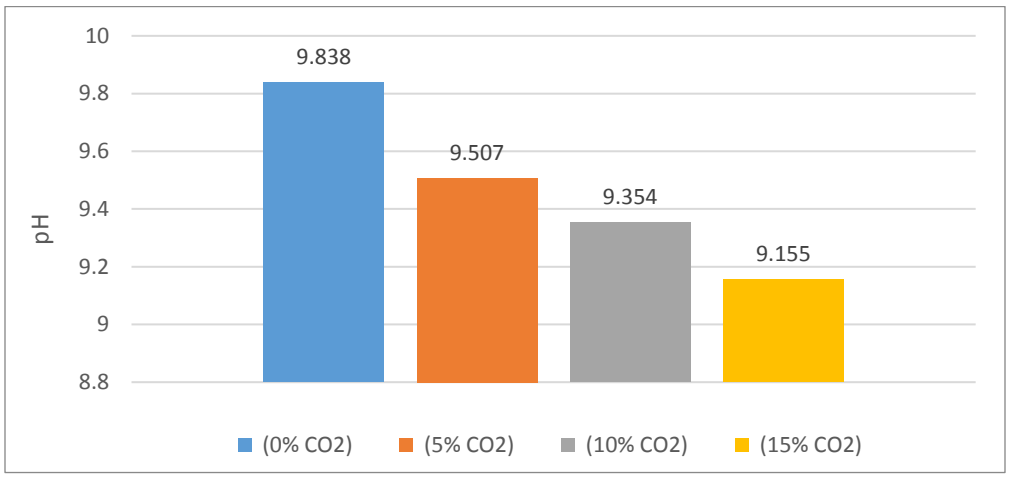

Figure 4.5: average pH value for different CO_2 concentrations at 20C

According to Figure 4.5 when the algae solution injected with CO_2 [5, 10, 15%] the pH decrease indicating the buildup of inorganic matter in the water solution. If the algae concentration in the water sample is high enough to utilize this amount of organic matter the pH of the solution increase again, when a balance between CO_2 injection and up take is established the pH variation decrease and stabilize. As it can be seen in the figure the pH variation for the algae culture injected with 5 % CO_2 is less than the cultures injected with 10 and 15%. However, for all these culture the variation of pH is not significant enough to reach inhibition for the culture, suggesting that Sp.PL has the capacity to uptake CO_2 at this high CO_2 injection. Similar results has been reported by (Singh *et al.*, 2015) for mixed cultures of microalgae. The obtained result have shown that SP.PL can be effective in CO_2 capture. (Picardo *et al.*, 2013) showed that when the pH is in the range of 6.0 to 9.0, bicarbonate (HCO^{3-}) is the most common form of inorganic carbon present in solution, based on our experimental results it can be concluded that this form of carbon promotes active transport through microalgal cells. Therefore, as per the experimental

conditions, the mechanism involved in CO_2 uptake is active transport, due to the high pH values observed. For culture injected with 15 % CO_2 and resulted in a decrease in pH values, meaning that CO_2 uptake in these conditions may be performed through diffusion.

4.1.1.3 CO_2 bio-fixation rate:

The biofixation rate of CO_2 was calculated using the Equation 4 proposed by (Mortezaeikia *et al.*, 2016)

$$CO2\ biofixation\ rate = P_{overall} \times C_{carbon} \times \frac{M_{CO2}}{M_C} \quad (4)$$

Where $P_{overall}$: Biomass productivity (g/l.day), C_{carbon}: content of carbon in algae biomass ($CO_{0.48}H_{1.83}N_{0.11}P_{0.01}$), M_{CO2}: molar mass of CO_2, M_C: molar mass of carbon. Figure 4.6 shows the calculated biofixation rates under different CO_2 dosage (0, 5, 10 and 15%), and temperature of 20 ˚C.

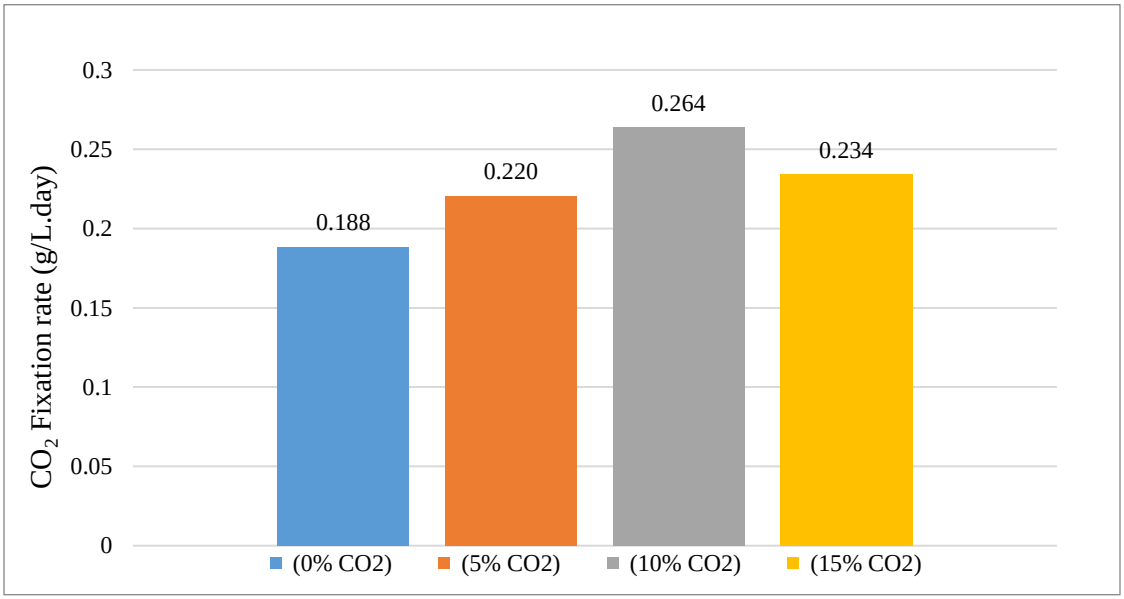

Figure 4.6:CO_2 fixation rate for different CO_2 concentration at 20 ˚C

As shown in Figure 4.6, SP.PL could grow with up to 15% CO_2 dosage. The used CO_2 dosage of 15 % did not show any negative effects on growing algal cells except the noticeable delay. As it can be seen in Figure 4.6 that CO_2 biofixation rate increase by increasing the CO_2 dosage from 0 to 10 %, and there is a small decease in the biofixation rate for algae culture injected with 15 % CO_2. The decrease in biofixation rate at 15% CO_2 injection is caused by the lower biomass productivity achieved at 15% CO_2 dosage. The obtained results demonstrating that the CO_2 can be utilized as carbon source for the growth of SP.PL and this species can be used successfully as a CO_2 capturing technology. Different studies have shown that a higher biomass productivity in any algal system is the result of more photosynthetic fixation of CO_2 (De Philippis e Vincenzini, 1998; Yang e Gao, 2003). The results reported in this study are in good agreement with the results obtained by (Singh *et al.*, 2005), who showed that prior pre-adaption of algae on low concentration of CO_2 can help algal cells overcome the physiological stress induced by high CO_2 dosage. This seems to be true as in our case, SP.PL was cultivated under very low CO_2 concentration before used in the experiments. In addition, the CO_2 biofixation rate reported in the present study are higher than the values reported in literature for SP.PL and other strains. (Singh *et al.*, 2005), showed that the maximum CO_2 bio-fixation value of 0.678 g CO_2/ L. d was observed by Spirulina at a CO_2 injection dose of 6%. Similarly, Scenedesmus sp. and Chlorella sp injected with of 6%. CO_2 showed a maximum CO_2 bio-fixation rate of 0.623 and 0.453 gCO2/ L d, respectively. Increasing the CO_2 dosage led to a decrease in bio-fixation rate of different algal strains. The CO_2 biofixation rates for Chlorella sp., Scenedesmus sp. and Spirulina sp. were at 24% CO_2 dosage were 0.221, 0.203 and 0.217 gCO2/L.d, respectively.

4.1.2 CO_2 capture at 25 ˚C:

4.1.2.1 algae growth:

Figure 4.7 shows the growth patterns of SP.PL (measured at OD_{680}) under different CO_2 dosage and at temperature of 25 ˚C. Results are average of 2 replicate calculated at 95% confidence level.

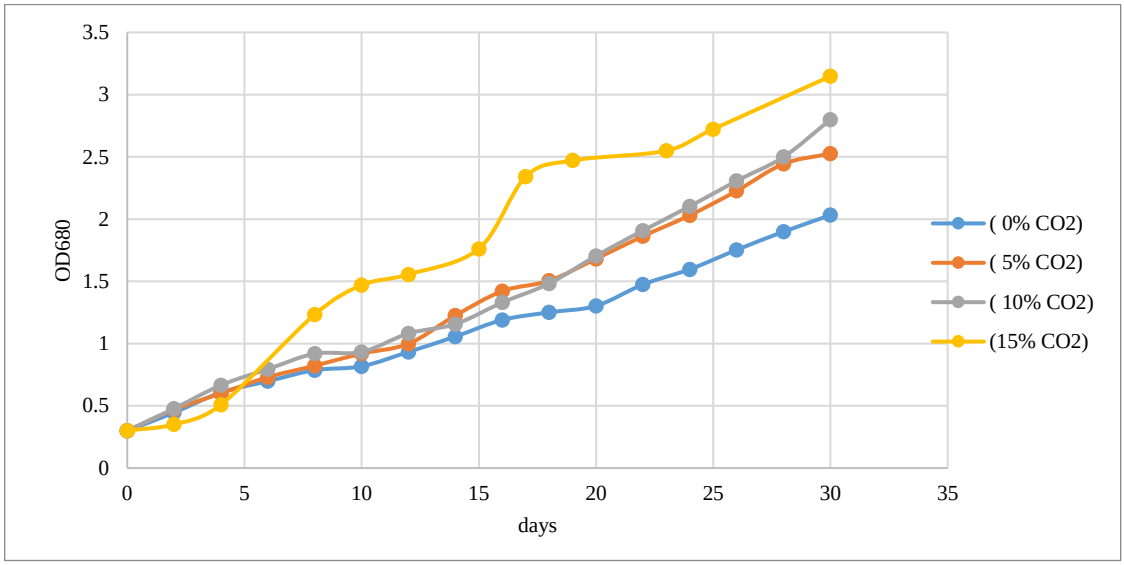

Figure 4.7: SP.PL growth under different CO_2 concentrations at 25˚C

It was noticed during the experiments at 25˚C that the growth patterns of SP.PL are the same as growth patterns at 20˚C. The growth patterns of SP.PL at 20˚C injected with different dosage of CO_2 follow the exact same trend except for the sample injected with 15% CO_2, which showed lower growth rate. After the sixth day, the sample injected with CO_2 dosage of 15% showed the highest growth reaching an OD of 3.15 A.U , followed closely by samples injected with CO_2 dosage of 10% and 5% at 2.80 and 2.53 A.U, respectively. Control sample [0% CO_2 injection] achieved the lowest growth of 2.0 A.U. It was noticed that sample injected with 15% CO_2 was able to improve much faster compared to the growth pattern under 20˚C. From Figure 4.7 its noticed that under 25˚C sample injected with 15% was able to achieve the highest growth starting

from day 6 compared to day 18 at 20 ˚C, which indicates that SP.PL was able to adapt better with higher CO_2 concentration at 25˚C. Figure 4.8 represents the summary of the growth rate of SP.PL under different CO_2 injection dosage.

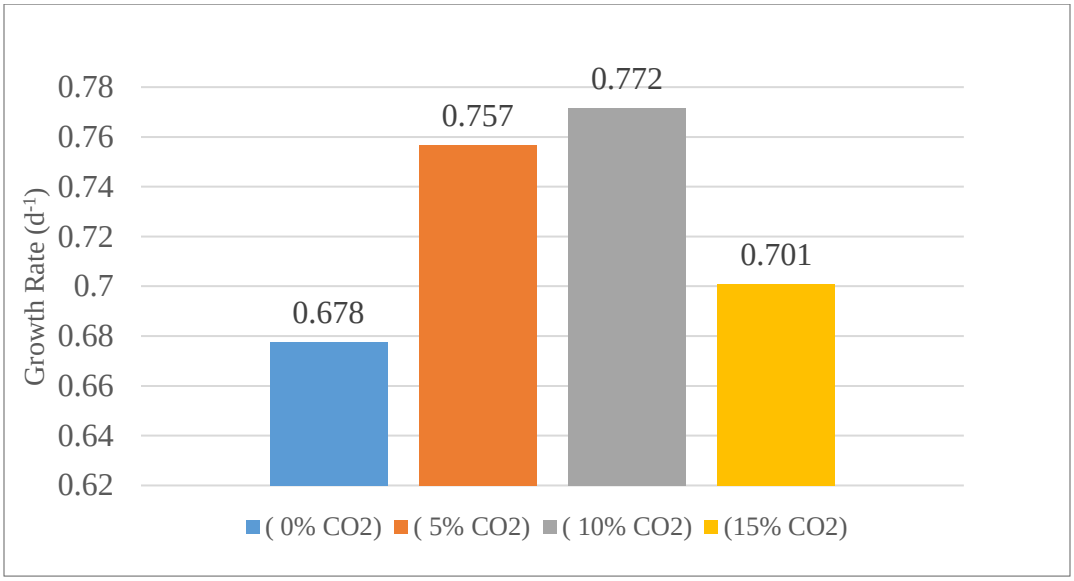

Figure 4.8: calculated growth rate under different CO2 concentrations at 25 ˚ C

The growth pattern of SP.PL in this set of experiments didn't show lag and stationary phases, the optical density showed a continues increase from the first day to the final day of incubation (day 30). The highest growth rate was reported for samples injected with a CO_2 dosage of 10%, followed by samples injected with a CO_2 dosage of 5%, 15% and 0%, respectively. The calculated growth rates were 0.772, 0.757, 0.701 and 0.678 d-1 for samples injected with a CO_2 dosage of 10%, 5%, 15% and 0%, respectively. The lower Growth rate reported for the 15% is caused by the growth delay during the first six days compared to the other samples. The growth rate values are very close to the values reported at 20˚C, it's clear that increasing the CO_2 dosage will increase the growth rate up to 10% CO_2 dosage. The 15% CO_2 although had much better

adaptation at 25˚C compared to 20˚C, the unbalanced growth during the first 6 days affected the overall growth rate for this sample. Figure 4.9 shows the biomass productivity for SP.PL at 25˚C

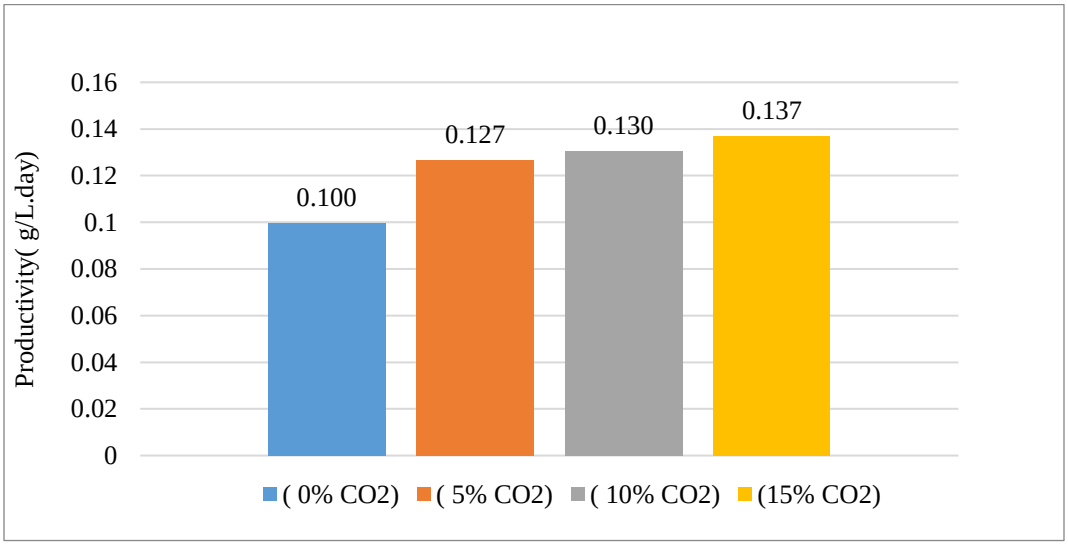

Figure 4.9: biomass productivity for different CO_2 concentration at 25˚C

There is a linear relationship between the biomass productivity and the injected amount of CO_2. As the CO_2 dosage increase the biomass productivity increase. The highest biomass productivity was observed for algae culture injected with 15% CO_2 followed by cultures injected with 10%, 5% and 0% respectively. The reported biomass productivities were 0.137, 0.130, 0.127 and 0.10 $gL^{-1}.day^{-1}$, respectively. The effect of the lower adaptation time of SP.PL at 25˚C can be seen in Figure 4.9 since the 15% sample could achieve the highest biomass productivity at 25˚C unlike the experiments at 20˚C where the 10% sample had the highest Biomass productivity.

4.1.2.2 pH:

Like the growth under 20°C, the algal solution pH was left to evolve freely but reported every day. Figure 4.10 shows the evolution of pH for solutions injected with a CO_2 dosage of 0, 5,10 and 15% at 25°C. Results are average of 2 replicate calculated at 95% confidence level.

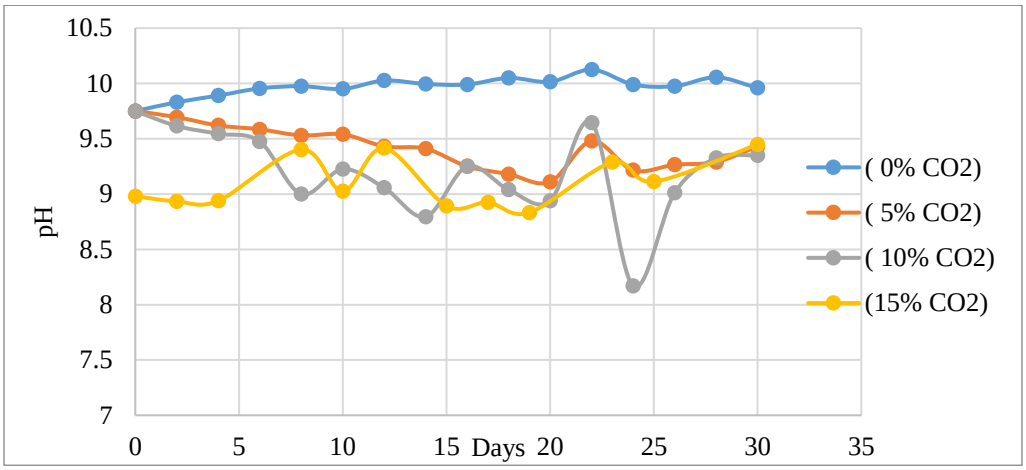

Figure 4.10: pH change during the experiment for different CO_2 dosage at 25°C

Control sample showed negligible pH variation, the pH of this culture ranged from 9.75 to 9.96, with an average value of 9.97. Other cultures injected with higher CO_2 dosage showed a noticeable decrease in the solution pH. The pH of the culture decreased gradually from 9.971 to 9.099 for the samples injected with 5%, 10%, and 15% CO_2 (see Figure 4.11). The obtained decrease in culture pH can be related to the changes in CO_2 mass transfer rate due to the changes in CO_2 concentration in the gas phase and the concentration of algae in the growth medium. As discussed above, to achieve balanced pH the concentration of algae in the growth medium should be enough to utilize all the CO2 gas supplied to the culture. The small variation in indicates that the concentration of algae in the medium is not enough to utilize all the supplied CO2.

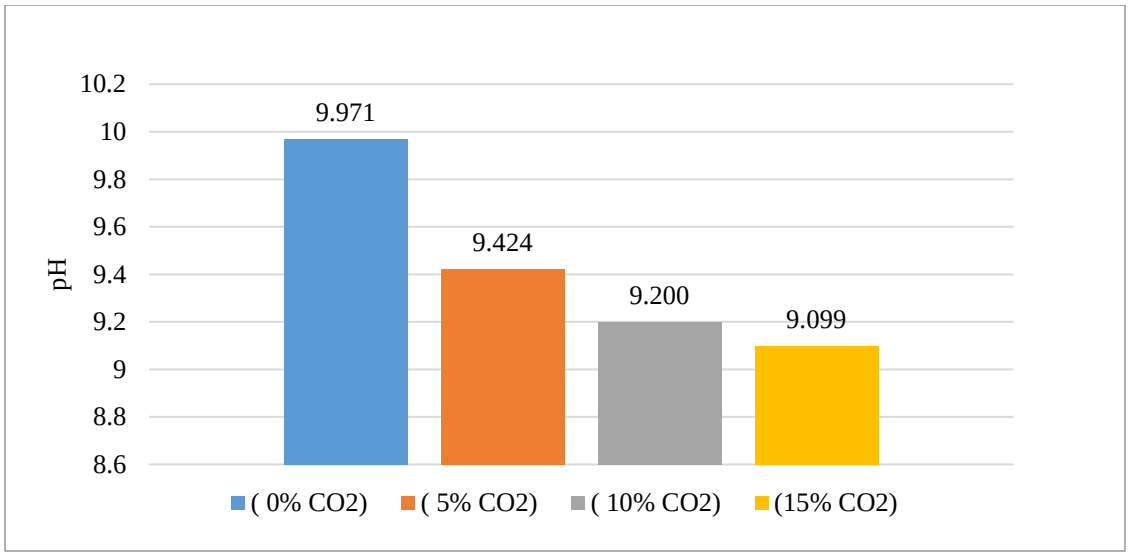

Figure 4.11: average pH value for different CO2 concentrations at 25C

4.1.2.3 CO_2 bio-fixation:

Figure 4.12 shows the biofixation rates under different CO_2 dosage (0, 5, 10 and 15%) at 25°C.

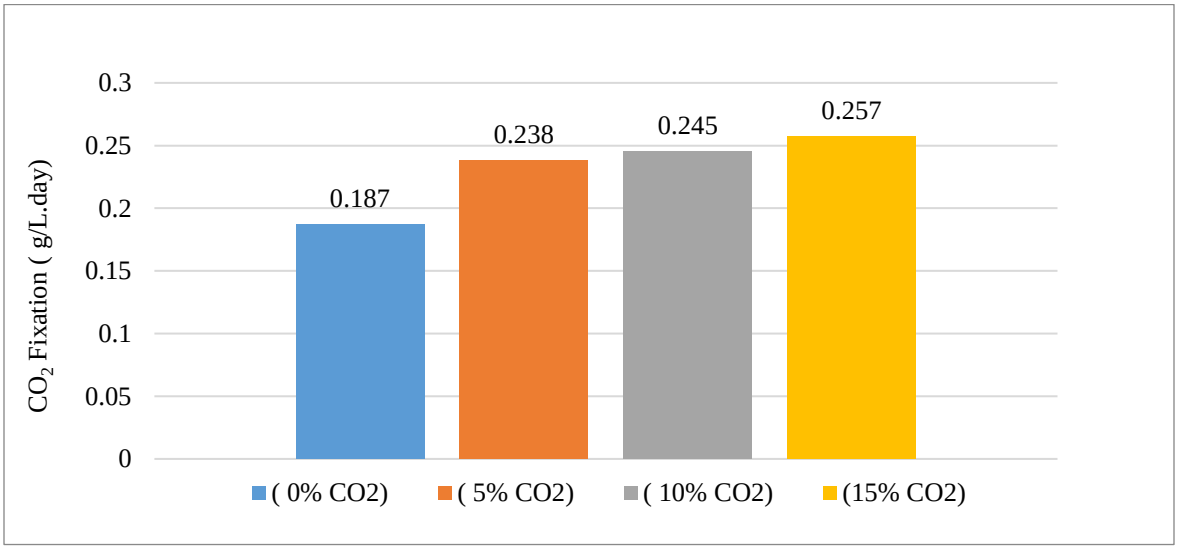

Figure 4.12: CO2 fixation rate for different CO2 concentration at 25°C

The obtained results showed that sample injected with 15% CO_2 achieved the highest CO_2 fixation rate at 0.257 $g.L^{-1}day^{-1}$ followed by 0.245, 0.238 and 0.187 $g.L^{-1}day^{-1}$ for samples injected with CO_2 concentrations of 10%, 5% and 0% respectively. Comparing the results at 20

and 25 ˚C indicate that increasing the temperature didn't show significant improve in the CO_2 fixation rates except for the sample injected with 15% CO_2. The CO_2 bio-fixation rate at 25 ˚C for the culture injected with 15 % CO_2 was found to be 8.9% higher than CO_2 bio-fixation at 20 ˚C.

4.1.3 CO_2 capture under 30 C:

4.1.3.1 Algae growth:

Figure 4.13 shows the growth patterns of SP.PL (measured at OD_{680}) under different CO_2 dosage [0, 5, 10 and 15%] and at temperature 30˚C.

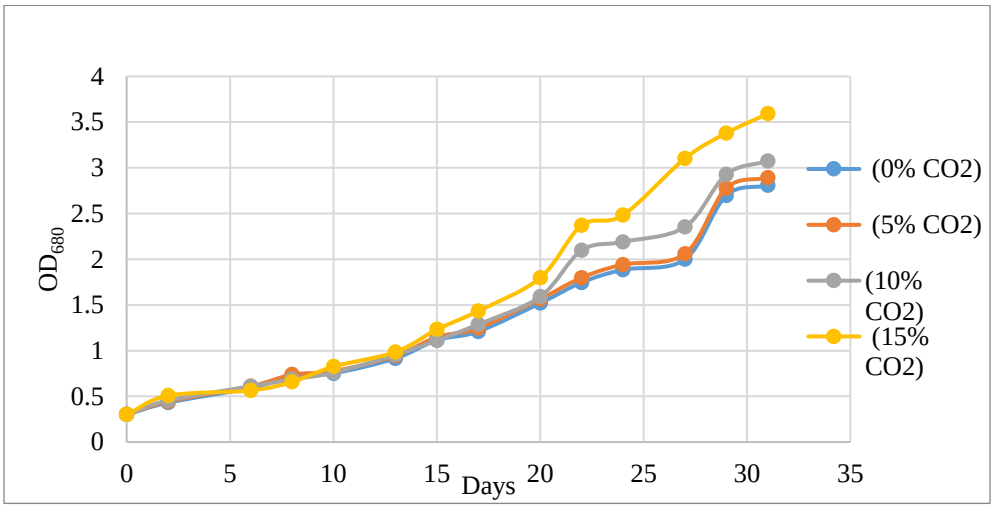

Figure 4.13: SP.PL growth under different CO_2 concentrations at 30˚C

Unlike the growth patterns of SP.PL under 20 and 25˚C it was noticed that the growth rate of all culture increase at the same rate. However, after day 13, cultures started to show variation in the growth, and culture injected with CO_2 dosage of 15% showed the highest growth. The reported maximum OD_{680} were 3.59, 3.07, 2.89 and 2.81 A.U for cultures injected with 15, 10, 5 and 0 %, respectively. The obtained trend suggest that all cultures were able to balance the supplied

CO_2 dosage. Figure 4.14 represents the summary of the growth rate of SP.PL under different CO_2 injection dosage at 30˚C.

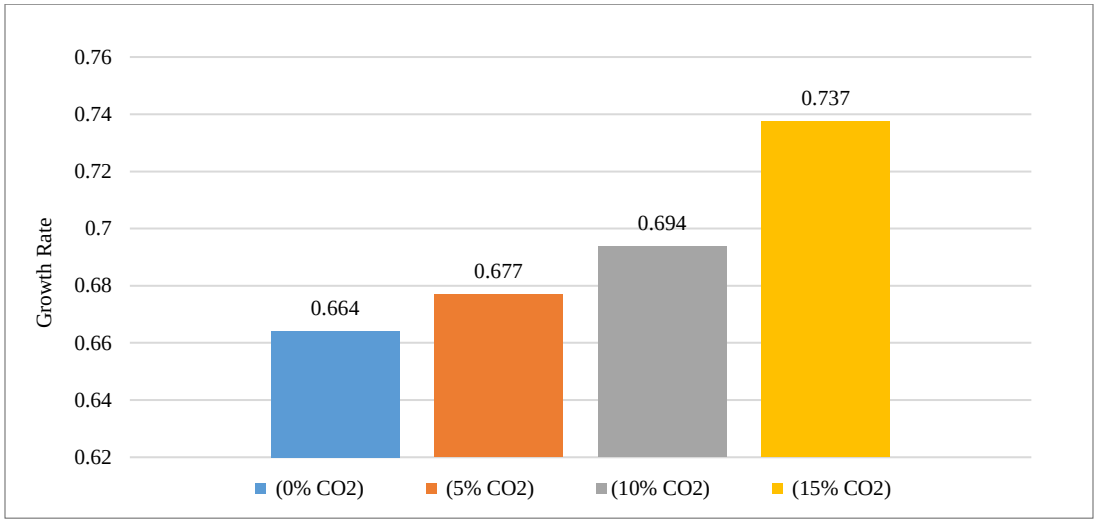

Figure 4.14: calculated growth rate under different CO2 concentrations at 30 ˚C

The highest growth rate was reported for samples injected with a CO_2 dosage of 15%, followed by samples injected with a CO_2 dosage of 10%, 5% and 0%, respectively. The calculated growth rates were 0.737, 0.694, 0.677 and 0.664 d^{-1} for samples injected with a CO_2 dosage of 15%, 10%, 5% and 0%, respectively. Figure 4.14 shows that SP.PL under 30 ˚C achieved a liner relation between the CO_2 % dosage and the calculated growth rates, which was not attained under experiments conducted at 20 and 25 ˚C. The dry cell weight of SP.PL was used to calculate the biomass productivity using a predetermined factor (see equation 2). Figure 4.15 shows the biomass productivity for SP.PL under different CO_2% dosage at 30 ˚C.

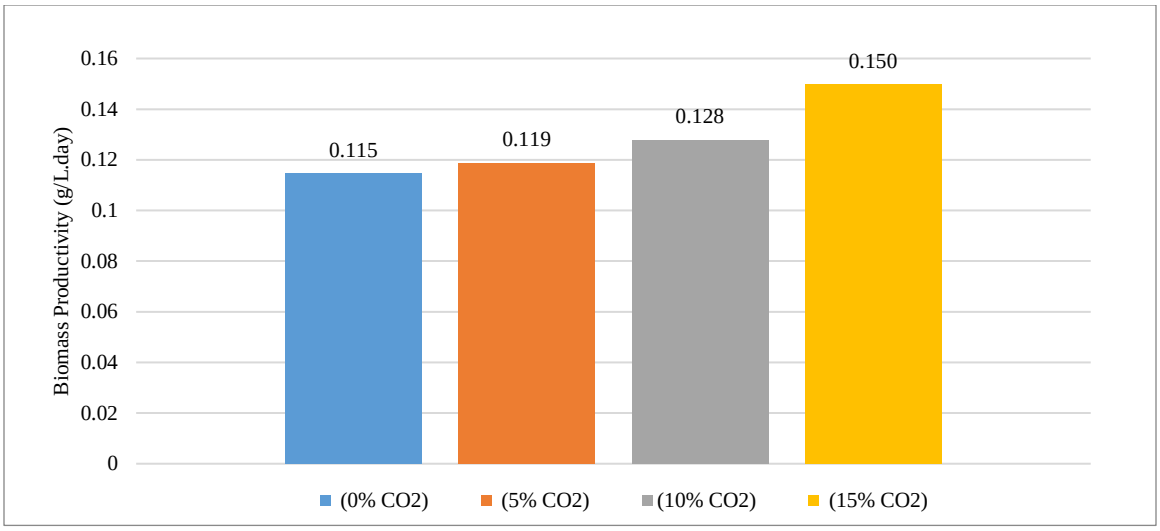

Figure 4.15: biomass productivity for different CO_2 concentration at 30˚C

Similar to the biomass productivity under 20 and 25˚C it can be seen in Figure 4.15 that there is a linear relationship between the biomass productivity and the injected amount of CO_2. As the CO_2 dosage increase the biomass productivity increase. The highest reported biomass productivity was for the 15% CO2 injection at 0.150 $gL^{-1}.day^{-1}$ followed by 0.128, 0.119 and 0.115 $gL^{-1}.day^{-1}$ for samples injected with 10%, 5% and 0% respectively. The effect of the higher temperature showed an improvement on the biomass productivity for the sample injected with 0 and 15% CO_2 at 0.115 and 0.150 compared to 0.10 and 0.137 respectively.

4.1.3.2 pH:

Figure 4.16 shows the evolution of pH for solutions injected with a CO_2 dosage of 0, 5,10 and 15% at 30˚C.

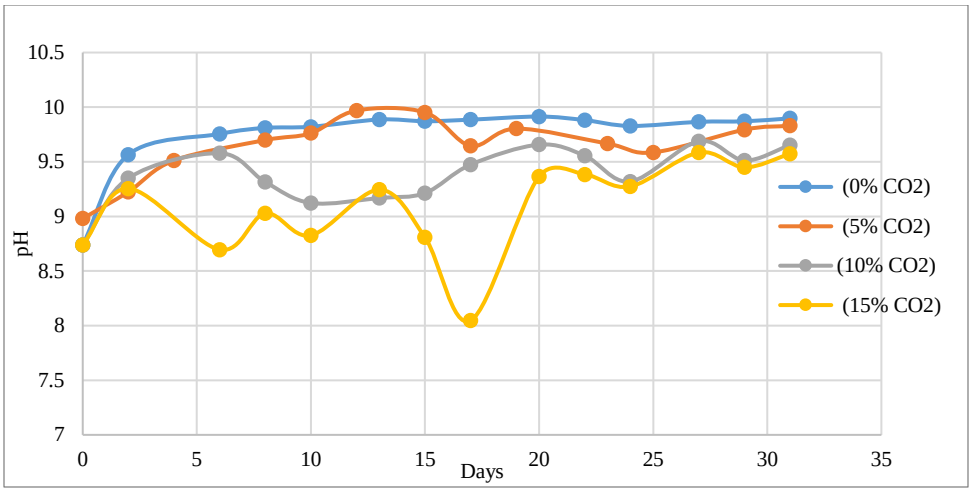

Figure 4.16: pH change during the experiment for different CO_2 dosage at 30°C

Figure 4.16 shows that control samples [0% CO_2 injection] showed noticeable pH variation, the solution pH ranged from 8.738 to 9.89, with an average value of 9.756. All other samples injected with CO_2 dosage in the range 5%-15% showed a noticeable decrease in the solution pH. the average pH value for the culture decreased gradually from 9.756 to 9.091 for the samples injected with 5%, 10%, and 15% CO_2 as can be seen in Figure 4.17. It was noticed from Figure 4.17 that the temperature didn't affect the average pH values [reducing pH value], which is believed to be because of the higher growth achieved under 30°C which led to more CO_2 consumption and higher pH values.

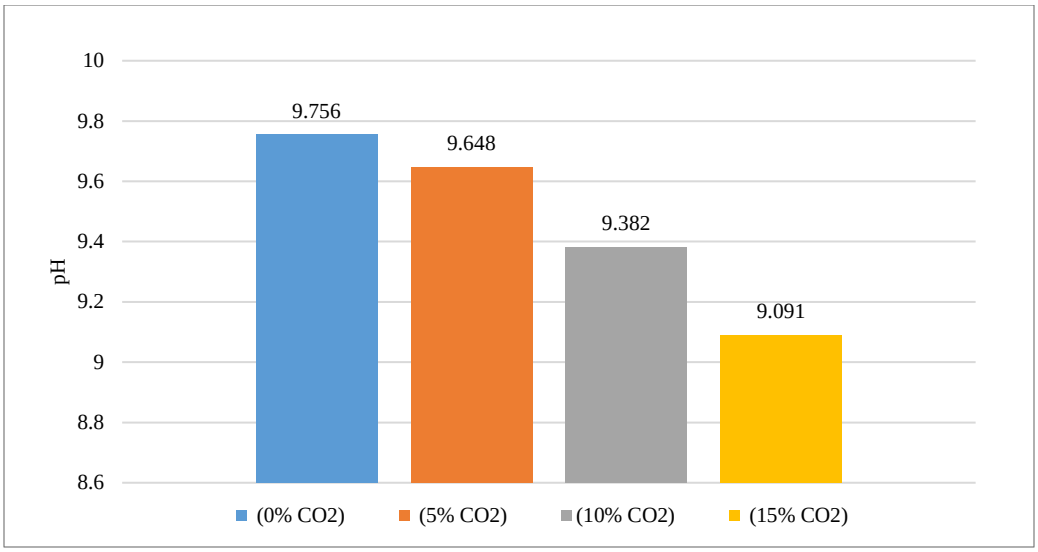

Figure 4.17: average pH value for different CO_2 concentrations at 30C

4.1.3.3 CO_2 Bio-fixation rate:

Figure 4.18 shows the calculated biofixation rates under different CO_2 dosage (0, 5, 10 and 15%), and temperature of 30˚C.

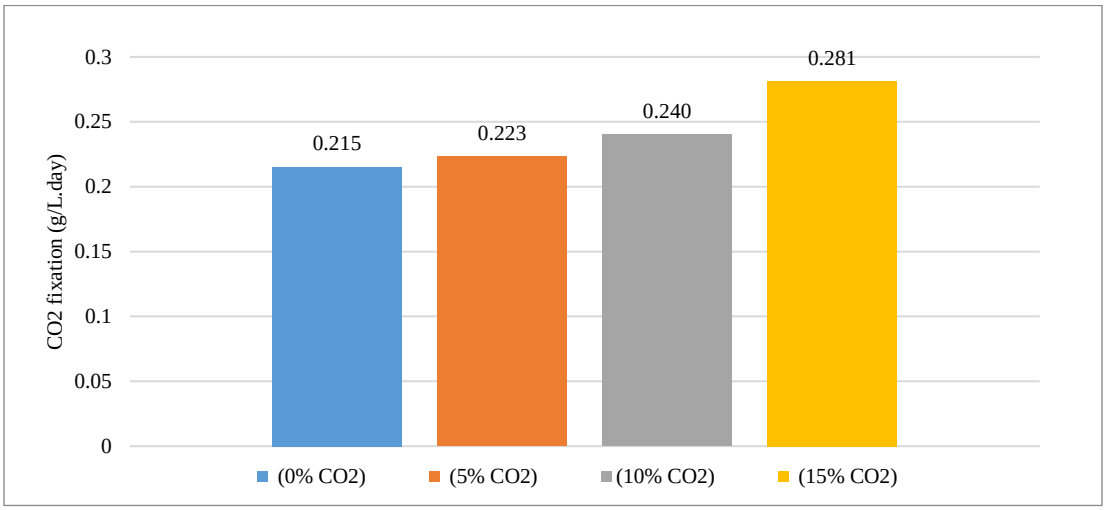

Figure 4.18: CO2 fixation rate for different CO_2 concentration at 30˚C

The obtained results showed that sample injected with 15% CO_2 achieved the highest CO_2 fixation rate at 0.281 $g.L^{-1}day^{-1}$ followed by 0.240, 0.223 and 0.215 $g.L^{-1}day^{-1}$ for samples injected with CO_2 concentrations of 10%, 5% and 0% respectively. Comparing the results at 30

and 25°C (0.257, 0.248, 0.238 and 0.187 $g.L^{-1}day^{-1}$), it's clear that increasing the temperature didn't show significant improvement on bio-fixation rate. Table 4.1 presents a summary of results obtained at the three temperatures (20, 25 and 30°C).

Table 4.1 : Summary of pH, Max OD, growth rate, biomass productivity and CO_2 fixation rate for temperatures of 20, 25 and 30°C

Variable	**20 C**				**25 C**				**30 C**			
CO_2 % (V/V)	**0%**	**5%**	**10%**	**15%**	**0%**	**5%**	**10%**	**15%**	**0%**	**5%**	**10%**	**15%**
Average pH	9.83	9.50	9.35	9.15	9.971	9.424	9.20	9.099	9.756	9.648	9.382	9.091
Max OD_{680}	1.93	2.36	2.73	2.99	2	2.53	2.8	3.15	2.81	2.89	3.07	3.59
Growth Rate	0.67	0.72	0.75	0.67	0.678	0.757	0.772	0.701	0.664	0.677	0.694	0.737
Biomass Productivity	0.10	0.11	0.14	0.12	0.10	0.127	0.130	0.137	0.115	0.119	0.128	0.150
CO_2 fixation	0.2	0.220	0.264	0.234	0.187	0.238	0.245	0.257	0.215	0.223	0.24	0.281

Although the maximum OD_{680} was obtained at 30ºC and 15% CO_2 injection, the highest growth rate was obtained at 25°C and 10% CO_2 injection The pH of algae culture was strongly related to the growth rate and temperature. At 25°C the average pH value for all sample injected with CO_2 were lower compared at 20°C, due to the imbalance in the CO_2 injection and SP.PL uptake of CO_2 because of the mass transfer or temperature limitation. In other words, SP.PL was not able to consume all the added CO_2 to the culture. At 30°C the pH values where higher due to the higher growth achieved at 30°C, which meant that more CO2 was removed and the culture pH increased. The highest biomass productivity was 0.150 $g.L^{-1}.d^{-1}$ obtained at 30°C and 15% CO_2 which led also to the highest CO_2 fixation rate of 0.281 $g.L^{-1}day^{-1}$ at the same conditions.

4.2 CO_2 Capture under Large-Scale (Pilot plant):

The objective of this part was to study the performance of SP.PL in capturing CO_2 at large-scale outdoor PBR. Experiments were carried out at different temperatures average values of 25.3 and 21.6 ˚C, daily CO_2 injection dosage of 5% and 10% and natural sunlight.

4.2.1 Algae growth:

Figure 4.19 shows the growth patterns of SP.PL under different CO_2 dosage of [5% and 10%].

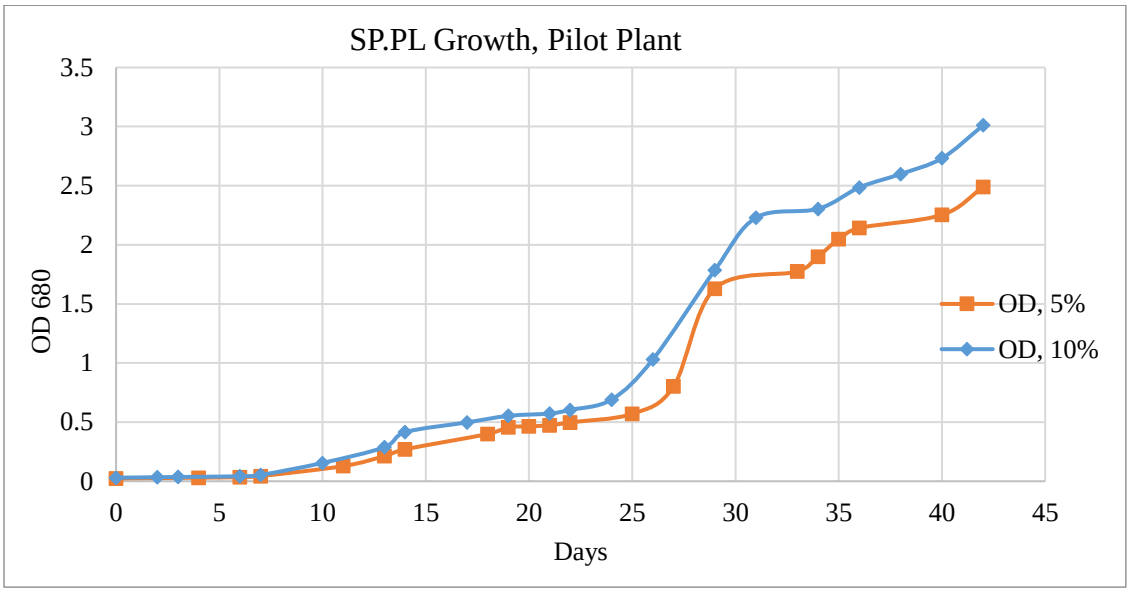

Figure 4.19: SP.PL growth under Large-scale and different CO_2 concentrations.

It was observed throughout these experiments that the growth patterns of SP.PL were characterized by a lag phase that lasted till day 7 and an extended exponential growth phase that starts directly after day 7. In addition, during the 42 days of incubation, stationary phase was not observed. The growth patterns of SP.PL during the first seven days, under all experimental conditions, follow the exact same trend. After the seventh day, samples started to show variation in the growth, and the sample injected with CO_2 dosage of 10% showed the highest growth rate reaching an optical density of 3.01, followed by sample injected with CO_2 dosage of 5% with an

optical density of 2.489 A.U. The average growth rates for SP.PL in pilot plant testing are presented in Figure 4.20

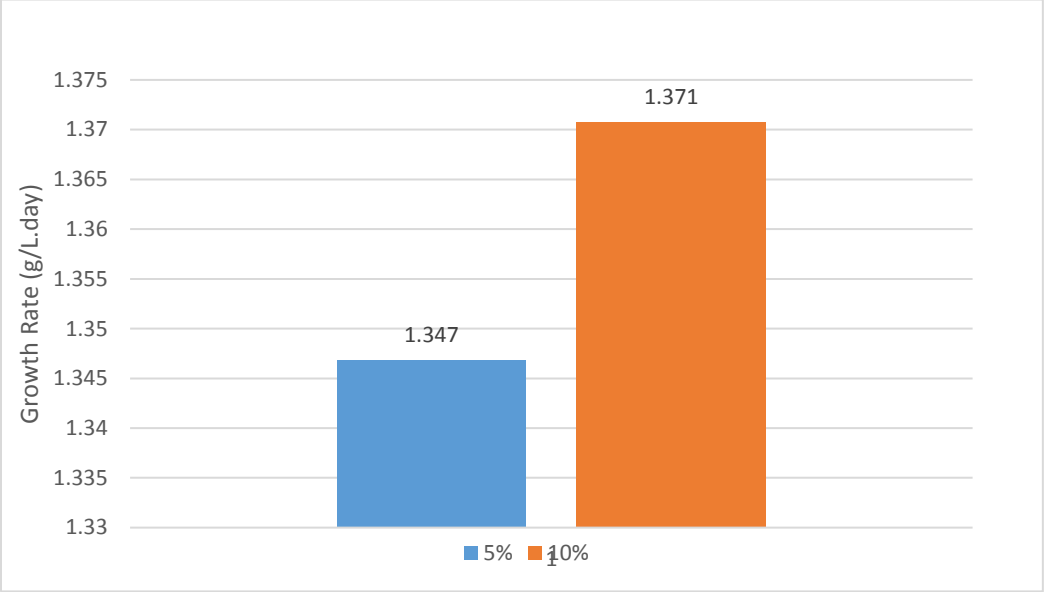

Figure 4.20: calculated growth rate under large-scale and different CO_2 concentrations

As the growth pattern of SP.PL in these experiments showed a lag phase for 7 days, the growth rates were calculated based on the growth time from day 7 to day 42 [i.e. during the exponential growth phase]. It can be seen in Figure 4.20 that the highest growth rate was reported for samples injected with a CO_2 dosage of 10%, followed by the sample injected with a CO_2 dosage of 5%. The calculated growth rates were 1.37 and 1.35 d^{-1} respectively. The calculated growth rates in pilot plant PBR injected with the same CO_2 dosages were noticeably higher than that growth rates in lab-scale PBR. Figure 4.21 shows the biomass productivity for SP.PL in pilot plant PBR injected with 5% and 10% CO_2 dosages.

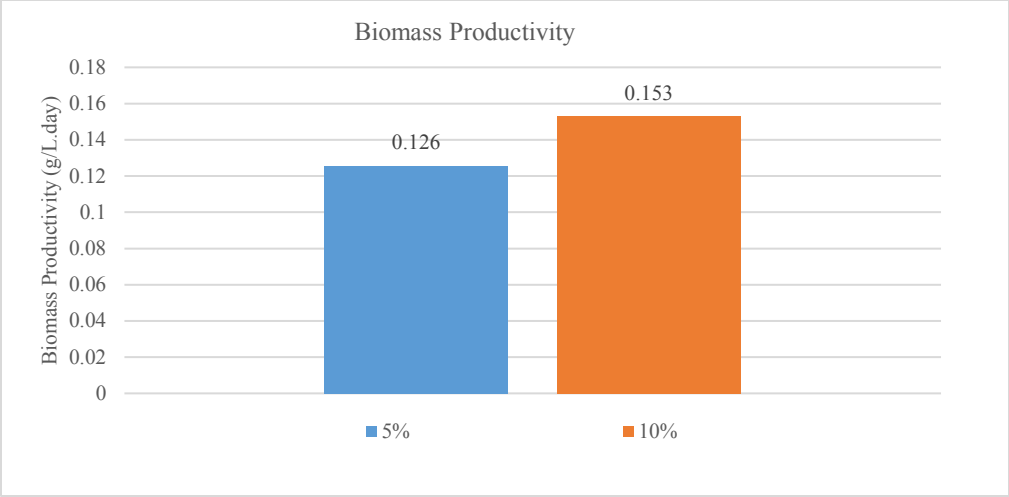

Figure 4.21: biomass productivity under Large-scale for different CO_2 concentration

it can be seen in Figure 4.21 that SP.PL under large-scale conditions could achieve a linear relationship between the biomass productivity and the injected amount of CO_2. Like the reported biomass productivities under lab-scale experiments when the CO_2 dosage increase the biomass productivity increase. The calculated biomass productivities were 0.126 $gL^{-1}.day^{-1}$ for the sample injected with 5% CO_2 and 0.153 $gL^{-1}.day^{-1}$ for the sample injected with 10% CO_2.

4.2.2 pH:

The change of solutions pH in the pilot plant was followed during the life time of these experiments. The algal solution pH was left to evolve freely but reported with every optical density measurement. Figure 4.22 shows the evolution of pH for solutions injected with a CO_2 dosage of 5 and 10%.

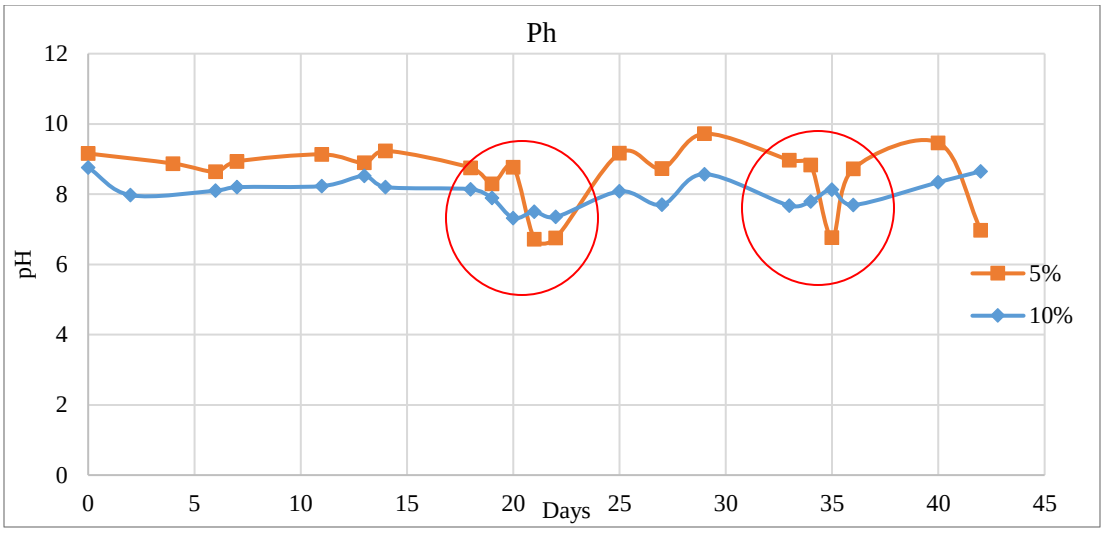

Figure 4.22: pH change during large-scale experiments

Figure 4.22 shows that both samples showed fluctuation in the pH value, which is believed to be because of the CO_2 injection and temperature variation. Results are average of 2 replicate calculated at 95% confidence level. The sample injected with 5% CO_2 showed a variation in pH in the range from 9.16 to 6.97 with an average value of 8.55, and the sample injected with 10% CO_2 showed a variation in pH value from 8.76 to 8.65 with average value of 8.04. Figure 4.23 shows the variation of temperature during the pilot plant testing. As indicated increasing the CO_2 dosage might lead to decrease in culture pH. However, increasing the culture temperature increase the growth rate and increase the CO_2 bio-fixation. For this reason, pilot plant experiment carried out at higher temperature showed more pH balance.

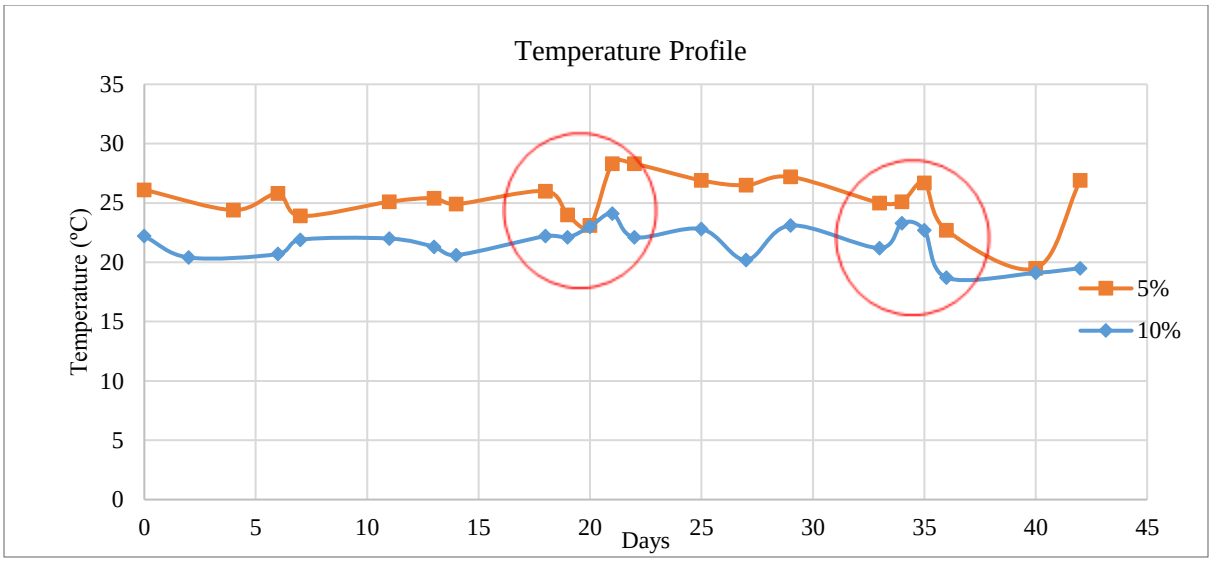

Figure 4.23: Temperature profile for CO2 injection of 5 and 10%

4.2.3 CO_2 bio-fixation rate:

The biofixation rate of SP.PL was calculated to estimate the performance of SP.PL in capturing CO_2 under large-scale and outdoor conditions. The biofixation rate of CO_2 was calculated using equation 4 mentioned in section 4.1.13. Figure 4.24 shows the calculated biofixation rates under CO_2 dosages of 5 and 10%.

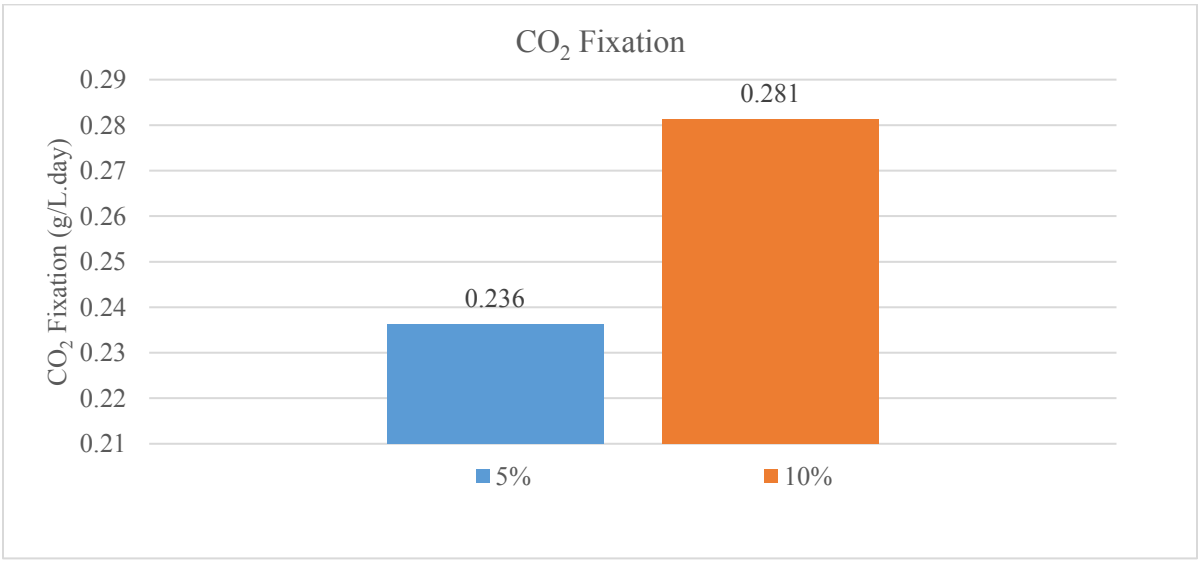

Figure 4.24: CO2 fixation rate under large-scale for different CO2 concentrations

As shown in Figure 4.24 algae cultures injected with 10% CO_2 achieved higher CO_2 bio-fixation rate than cultures injected with 5 % CO_2. The bio-fixation rate were 0.281 and 0.236 $g.L^{-1}day^{-1}$ for cultures injected with 10 and 5% CO_2, Respectively. Since the average temperatures for the pilot plant PBR were 25.3 and 21.6°C, Table 4.2 compares the results obtained in pilot plant PBR to those obtained in the lab-scale PBR at 20 and 25°C.

Table 4.2: Pilot plant PBR vs lab-scale PBR

Variable	***Lab-Scale PBR***		***Pilot Plant PBR***	
Temperature	20 C	25 C	21.6	25.3
CO_2%	5%	10%	5%	10%
Average pH	9.507	9.2	8.65	8.04
Max OD_{680}	2.36	2.8	2.489	3.01
Growth Rate	0.724	0.772	1.347	1.371
Biomass Productivity	0.117	0.13	0.126	0.153
CO_2 fixation	0.22	0.245	0.236	0.281

Table 4.2 shows that under almost the same conditions SP.PL in pilot plant PBR was able to achieve better performance compared to the Labe-scale PBR. The results indicate that there is a great potential for SP.PL to be cultivated under large-scale conditions. It's worth mentioning that SP.PL was not able to grow in the pilot plant PBR under 0% CO_2 injection, due to algae accumulation on the walls of pilot plant PBR, which lead to SP.PL death due to excessive heating and limited light surface, similar behavior was observed by (Santos *et al.*, 2015). It was notice during the experiment that injecting CO_2 to the system created rapid mixing which helped release the sticking algae. After noticing the effect of CO_2 injection, the system was modified by adding 6 more CO_2 injection ports. In other words, each vertical tube in pilot plant PBR had a CO_2 injection port and the injection time was divided between the eight ports.

4.3 Nutrients Removal:

As indicated before green algae can be used as an advanced wastewater treatment technology to polish the effluent of any wastewater treatment plant (WWTP). In this case, green algae used to remove and reduce the concentrations of nutrient (ammonia and phosphorous) to a specific limit that permit the use of the treated wastewater in agriculture or safe discharge to surface water. SP. PL was used during this study to remove nutrient from secondary wastewater treatment plant. The concentrations of ammonia and phosphorus in this wastewater were 22 mg-N/L and 37.5 mg-P/L, respectively. The study of nutrient removal by SP.Pl was carried out at two temperatures (25and 30 ◦C). For each temperature, nutrient removal was evaluated under three different doses of CO_2 (0%, 5% and 10%). Experiment with no CO_2 addition was considered as a control experiment. Experiments were carried out in duplicate and average value were reported.

4.3.1 Nutrient removal at 25◦C:

4.3.1.1 Algae growth:

Algae growth was followed up by measuring the optical density (OD) of the wastewater during the incubation period. Figure 4.25 shows the evaluation of OD during the incubation period of SP.PL in wastewater at different CO_2 dosage and at temperature 25◦C

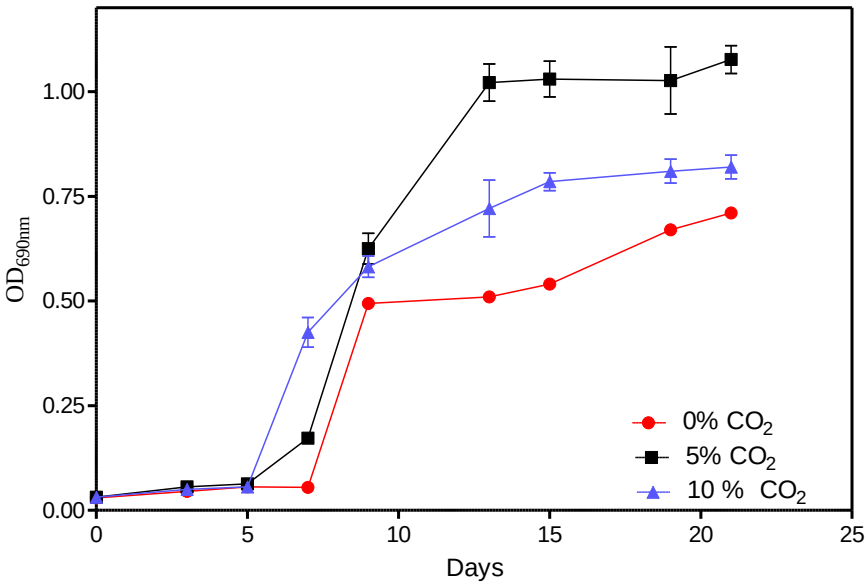

Figure 4.25: SP.Pl growth in wastewater at different CO_2 dosage and at temperature 25◦C

It can be seen in Figure 4.25 that SP.PL follow typical growth trend consisting of lag phase, exponential growth phase and stationary phase. No decay phase was observed during the 21 days incubation period. The lag phase for the three conditions are almost the same. However, it can be seen that the lag phase for control experiment (0% CO_2) was longer (7 days) than lag phase observed under 5 and 10% CO_2 injection. The growth phase was followed by exponential growth phase. Results showed that SP.PL cultivated with 5 % CO_2 showed higher exponential growth phase compared with SP.PL cultivated under 0 and 10 % CO_2. Overall, the growth of SP.PL at 5% CO_2 dosage showed the highest growth rate. It also can be noticed that increasing the % CO_2 in the gas injection line has no effect on the lag phase but affect the trends of the exponential phases for the same wastewater. The max OD_{680} recorded for each reactor were 0.71, 1.00 and 0.82 for culture injected with 0, 5 and 10 v/v% CO_2 respectively. A calibration curve was used to covert the OD_{680} to dry cell weight as shown in section 3.5.1. the calculated dry cell weights were 0.162, 0.239 and 0.185 g/L for samples injected with 0, 5 and 10% CO_2. The growth rate

for each culture was calculated using equation 3. Algae culture injected with 5% CO_2 achieved the highest growth rate at 0.689 $g.L^{-1}.day^{-1}$ followed by 0.677 and 0.536 $g.L^{-1}.day^{-1}$ for the 10 and 0% respectively.

4.3.1.2 pH and DO:

Figure 4.26 shows the evolution of dissolved oxygen (DO) and the pH during the treatment of the wastewater by green algae SP.PL under different CO_2 injection dose. All the reported values of OD and pH fluctuate around an average fixed value indicating that all the system are working under proper operational conditions. Fluctuation in these operational parameters are normal due to different reason such as change in wastewater chemistry, small variation in solution temperature and the presence of unexpected contaminates in the wastewater. It can be seen in Figure 4.26-A that the pH of the wastewater treated by SP.PL an injected with 0% CO_2 ranged from 8.6 to 8.9, with a final value stabilized at 8.9. When the same WW was treated with the same algae strain but with higher CO_2 dosage (5% and 10%), The pH decreased from 8.6 to 6.8 for solution injected with 5 % CO_2 and from 8.6 to 6.7 for solution injected with 10 % CO_2 (see Figure 4.26-B and Figure 4.26-C) .

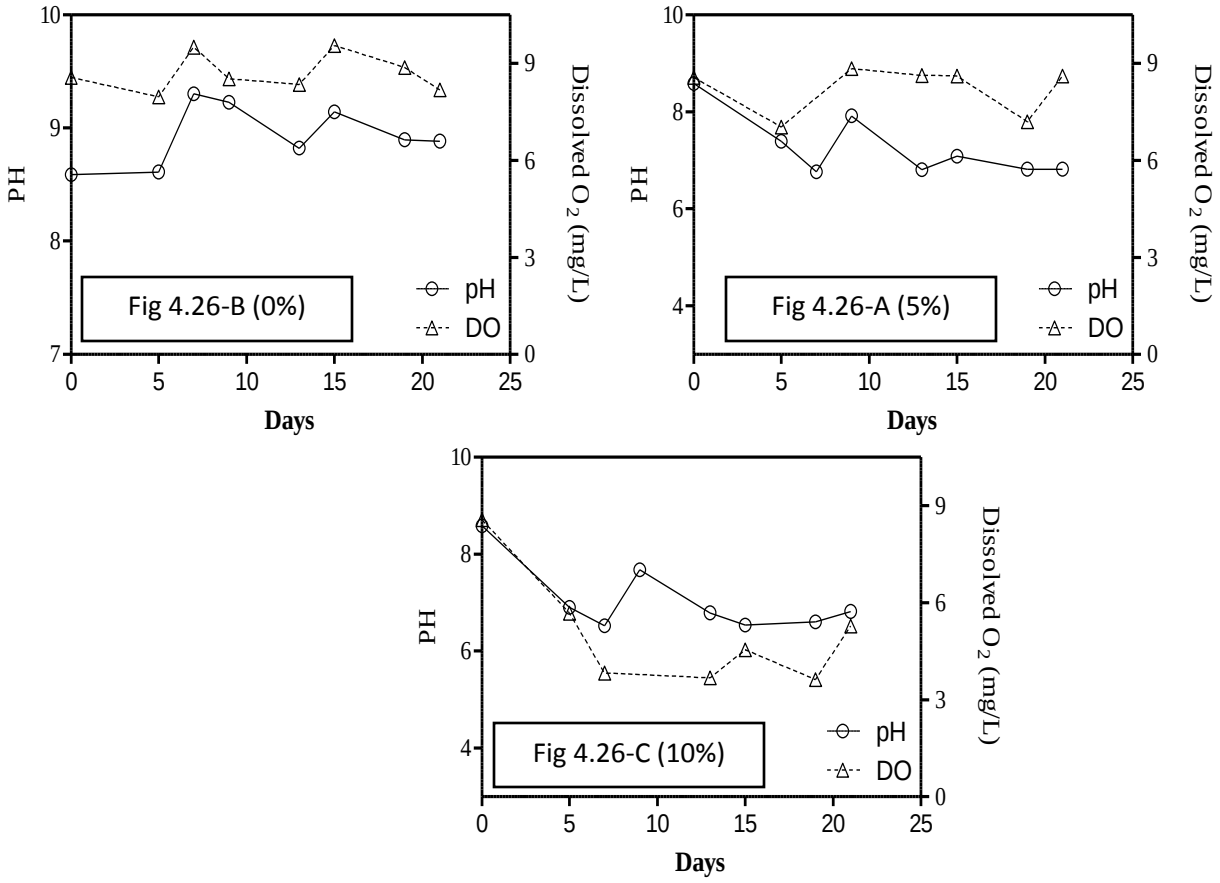

Figure 4.26: evolution of dissolved oxygen (DO) and the pH during the treatment of the wastewater by green algae SP.PL under different CO_2 injection dose

4.3.1.3 Ammonia removal (NH_4-N):

The potential of using SP.PL green algae as a nutrient removal technology was followed by studying the ammonia-nitrogen removal from WW under different CO_2 dosage. It is known that ammonia is considered as the most preferable inorganic nitrogen for microalgae. Ammonia removed from the WW can be utilized by the algae nitrogen in cell synthesis (Abdulsada, 2014). On other hand, regulations and wastewater treatment discharge restrictions put a limit on the permitted concentration of ammonia to be in the treated wastewater before discharge to surface

water and/or used for agricultural application. Being that said, nutrient removal by green algae can be considered as a post-treatment for the conventional WWTP to polish the remaining amount of the ammonia in the treated WW. Figure 4.27 shows the evaluation of ammonia and ammonia % removal obtained during the treatment of wastewater by SP.PL green algae under different CO_2 dosage.

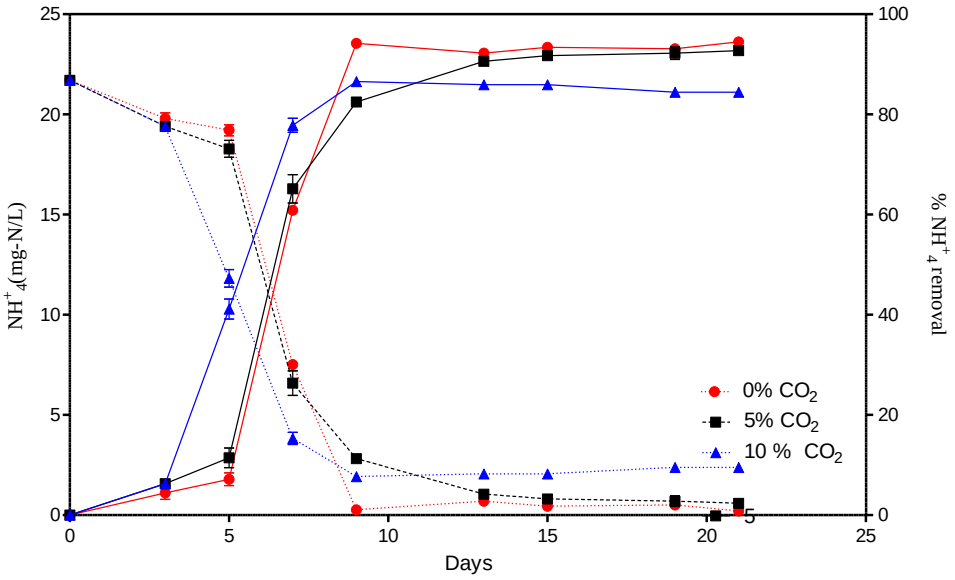

Figure 4.27: evaluation of ammonia and ammonia % removal obtained during the treatment of wastewater by SP.PL

For all experimental conditions, the concentration of NH_4^+-N-N dropped rapidly from 22 mg-N/L to less than 2.5 mg-N/L. In addition, it was observed that the major decrease in NH_4^+-N occurs during the first 9 day, after that the concentration remains almost constant. The short time required to decrease the concentration of ammonia suggest that the treatment process time can be cut off after 9 days, this of course will improve the economic feasibility of the post-treatment process. The performance of SP.PL in removing ammonia from wastewater was noticed to be dependent on the % CO_2 injection, with a general trend indicated that SP.PL perform better ammonia removal under low CO_2 injection dose. Experiments performed with 0 and 5% CO_2

injection showed a rapid decrease in ammonia concentration from an initial concentration of 22 mg-N/ to 0.20 and 0.60 mg-N/, respectively. Experiments performed with 10% CO_2 injection showed a decrease in ammonia concentration from an initial concentration of 22 mg-N/ to 2.50 mg-N/L. The % ammonia removals for experiments performed with 0, 5 and 10 % CO_2 were 94.5, 92.4 and 84.5%, Respectively. It can be concluded that that SP.PL can be used efficiently to remove ammonia from wastewater. It is known that ammonia can also be removed from WW by volatization. A conbtrol experiment was performed to follow up the decresae in ammonia concentraion as a results of volatization. The results showed that less than 5% of the ammonia was lost suggesting that the reported ammonia removals were all due to biological up take by green algae.

The concentration of nitrate and nitrite were also monitored durin the experiments to check if nitrate or nitrite can be genreated or consumed during ammonia removal process., All samples showed an increse of nitrate concentration to a value less than 3.5 mg/L. Nitrite concentration was also monitiored and all samples showed a decrease in nitrite concentration from 0.1 to 0.003. Figures showing the evolution of the concetrations of nitarte and nitrite during ammonai removal experiments can be found in Appendix A-1.

The results reported in this study disagree with the results reported by (Wang *et al.*, 2010) who showed that nitrite increase and nitrate decrease during the cultivation of Chlorella sp in different WW. (Wang *et al.*, 2010), indicated that nitrate can be assimilated by algae by mass transport of nitrogen compounds to algae cell followed by reduction reactions to produce ammonium in the chloroplast. In this case, nitrite is generated as a results of nitrate reduction to ammonium and it is possible that part of the nitrite produced was excreted into the media. In the present study, the increase of nitrite was not observed suggesting that most of the reduced nitrate was also utilized

by SP.PL. The results also may imply that SP.PL has more capacity to uptake nitrogen compound compared with Chlorella sp.

The percent ammonia removal efficiencies reported in this study are considered higher than the removals reported by (Aslan e Kapdan, 2006; Wang *et al.*, 2010; Wang e Lan, 2011),the reported ammonia removal were 68.4-82.8% by Chlorella sp and 72% by Chlorella vulgaris. (Gonçalves *et al.*, 2014) reported up to 100% removal of nitrogen.

4.3.1.4 Phosphorus removal:

The potential of using SP.PL green algae as a nutrient removal technology was followed by studying the Phosphorus removal from WW under different CO_2 dosage. Phosphorus presence in WW bodies is known to cause ecosystem disturbance due to algal bloom and illness (Jalal *et al.*, 2011). Using algae to deplete the phosphorus from WW before the discharge will offer an economic efficient solution and safer option for the environment. Soluble Phosphorus has two main mechanisms for removal which are; precipitation due to high pH and assimilation by microalgae (Abdulsada, 2014). Figure 4.28 shows the evaluation of phosphorus and phosphorus % removal obtained during the treatment of wastewater by SP.PL green algae under different CO_2 dosage.

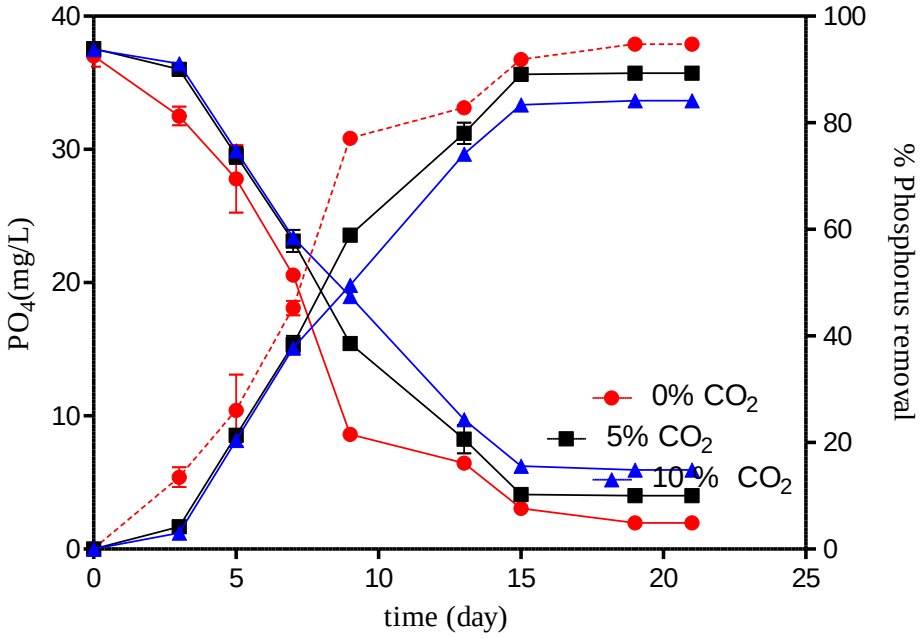

Figure 4.28: valuation of phosphorus and phosphorus % removal obtained during the treatment of wastewater by SP.PL

For all experimental conditions, the concentration of the total dissolved PO_4 (TP) dropped rapidly from 37.6 mg-PO_4/L to less than 6 mg-PO4/L. In addition, it was observed that the major decrease in PO4 occurs during the first 15 day, after that the concentration remains nearly constant. The performance of SP.PL in removing phosphorus from wastewater was noticed to be dependent on the % CO_2 injection, with a general trend indicated that SP.PL perform better ammonia removal under lower CO_2 injection. Experiments performed with 0 and 5% CO_2 injection showed a rapid decrease in phosphorous concentration from an initial concentration of 37 mg-N/ to 2 and 4 mg-N/, respectively. Experiments performed with 10 CO_2 injection showed a decrease in phosphorous concentration from an initial concentration of 37 mg-N/ to 6 mg-N/L. The % phosphorous removals for experiments performed with 0, 5 and 10 % CO_2 were 94.8, 89.3 and 84.2%, Respectively. From the high phosphorus removal achieved by Sp.PL, it can be concluded that that SP.PL can be used efficiently to remove phosphorous from wastewater. The obtained results agree with reported values from the litrature, (Rajkumara e Takriffa, 2015) reported a maximum phosphorus removal of 96.8% by SP.PL. (Zhu *et al.*, 2013) also reported 90-100% phosphorus removal from piggery wastewater by Chlorella zofingiensis. Other studies reported lower phosphorus removal ranging from 40 to 50% (Jalal *et al.*, 2011). As mentioned before Phosphorus has two main mechanisms for removal which are; precipitation due to high pH and assimilation by microalgae, after inspecting the pH profile for each sample it was found that assimilation by microalgae is the main mechanism of removal since the pH value never reached 11 which is required for the precipitation of phosphorus as reported by (Larsdotter, 2006)

4.3.1.5 COD uptake:

The potential of using SP.PL green algae as a nutrient removal technology was followed by studying the COD from WW under different CO_2 dosage. Several organic and inorganic pollutants exist WW bodies, which can be harmful to the environment. Organic compounds exist in various forms in the WW, but all have at least one carbon atom. The oxidation of the carbon atoms can be accomplished biologically or chemically which will produce carbon dioxide (Abdel-Raouf *et al.,* 2012). Microalgae typically use inorganic carbon source. The first choice for microalgae in this case SP.PL is CO_2 followed by bicarbonate (HCO3-) if CO_2 is not available, which requires carbonic anhydrase to convert it to CO_2. Microalgae can function differently under the environmental conditions; some species can grow under phototrophic or heterotrophic conditions. Under phototrophic microalgae consumes carbon in the form of CO2, while under heterotrophic microalgae consumes carbon in the form of dissolved organic carbon such as organic acids and acetate (Borowitzka, 1998). Figure 4.29 shows the evaluation of COD and COD % removal obtained during the treatment of wastewater by SP.PL green algae under different CO_2 dosage.

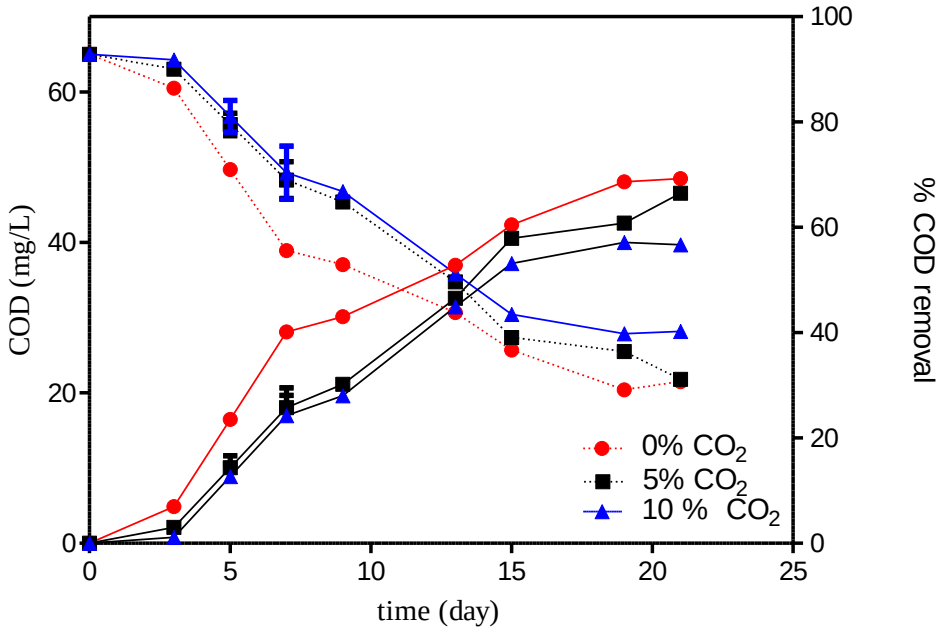

Figure 4.29: the evaluation of COD and COD % removal obtained during the treatment of wastewater by SP.PL

For all experimental conditions, the concentration of the COD dropped gradually from 65 mg-COD/L to less than 28.2 mg-COD/L during the 21 days of incubation. The performance of SP.PL in removing COD from wastewater was noticed to be dependent on the % CO_2 injection, with a general trend indicated that SP.PL perform better COD removal under lower CO_2 injection. Experiments performed with 0 and 5% CO_2 injection showed a decrease in COD concentration from an initial concentration of 65 mg-COD/L to 21.5 and 21.8 mg-COD/L, respectively. Experiments performed with 10% CO_2 injection showed a decrease in COD concentration from an initial concentration of 65 mg-COD/ to 28.2 mg-COD/L. The % COD removals for experiments performed with 0, 5 and 10 % CO_2 were 69.23, 66.49 and 56.68%. The obtained results agree with reported values from the literature, (Zhu *et al.*, 2013) reported COD removal efficiency ranging from 65 to 76% by Chlorella zofingiensis. (Tarlan *et al.*, 2002) showed that up to 58% of COD can be removed from the WW by mixed algal culture.

Since the experiments conducted at 30ºC follow the same trends, Table 4.3 presents the summary of nutrients removal obtained at 25 and 30ºC

Table 4.3:nutrints removal results at 25 and 30^{o}C

Variable	***25 C***			***30 C***		
	0%	**5%**	**10%**	**0%**	**5%**	**10%**
Average OD_{680}	0.385	0.522	0.389	0.41	0.69	0.56
Max OD_{680}	0.71	1	0.82	0.856	1.67	1.18
Average pH	8.934	7.343	7.053	9.042	7.86	7.51
(NH4-N) %	94.5	92.7	84.5	99.64	98.68	97.15
PO4%	94.76	89.33	84.15	85.57	84.40	80.04
COD %	69.23	66.49	56.68	43.10	40.8	36.3

SP.PL grown at 30ºC was able to achieve higher optical density under CO_2 injection of 0, 5 and 10%. Under both temperatures the 5% dosage achieved the highest optical density at 1.67 and 1.00 for the sample incubated at 30 and 25ºC respectively, similar results were obtained by (Yun e Lee, 1997; Gonçalves *et al.*, 2014). The culture pH followed the same trend noticed during the CO_2 capture experiments, the pH value for samples with 0% CO_2 injection increased with and average value of 8.93 and 9.04 at 25 and 30ºC respectively. All sample injected with CO_2 dosage of 5 and 10% under both temperature showed a decrease in pH value, this behavior is in agreement with the behavior reported by (Yun e Lee, 1997). Ammonia removal showed improvement at higher temperature, the highest removal was 99.64 obtained at 30C and 0% CO_2 injection, (Zimmo *et al.*, 2004) showed similar results when comparing the removal of nitrogen compounds at warm and cold temperatures . Phosphorus removal showed a decrease at higher temperature, the highest phosphorus removal was 94.76% obtained at 25ºC and 0% CO_2

compared to 85% at 30ºC COD removal also decreased at 30ºC, the highest COD removal was 69.23 obtained at 25ºC and 0% compared to 43.8% at 30C. Although SP.PL was successfully able to remove the nutrient from the WW, it was noticed that increasing the CO_2 concentration reduces the nutrients removal, similar results were obtained by (Gonçalves *et al.*, 2014), it showed that cultures with no CO_2 enrichment achieved higher nitrogen and phosphorus removal during the adaptation period compared to CO_2 enriched cultures which agrees with the results obtained in this study since most of nutrients were removed during the adaptation period.

Conclusion:

There is obviously a substantial opportunity for applying photo-bioreactor technology to the combined capture and fixation of carbon dioxide from processes discharging gases and the recovery of nutrients from wastewater sources. The system is considerably more complex than conventional biological treatment systems, as typically applied to wastewater treatment. This arises from the necessity to balance the input of carbon and nutrient from gas and aqueous streams to sustain the system biology. There are number of challenges to be met for combined CO_2 and nutrient mitigation by algal PBRs. Firstly, an appropriately robust microalgal strain must be selected which can (a) readily adapt to the wastewater and gaseous discharge environment, and (b) provide both effective nutrient removal and high biomass productivity. Secondly, there significant process control challenge must be met, since effective biological processing demands balancing of the carbon, nitrogen and phosphorus (the C:N:P ratio). PBRs potentially offer an energy-positive and low-waste technical option for combined CO_2 mitigation from flue gases and treatment of municipal and industrial wastewaters. SP.PL capability of carbon capture and nutrients removal was tested under different CO_2 dosage [0, 5, 10, 15%], Temperatures [20, 25, 30] and PBRs scale. In the lab-scale PBR, SP.PL was able to adapt and growth with up to 15% CO_2. At each temperature [20, 25, 30ºC] SP.PL was able to achieve higher growth at higher CO_2 concentration, but under 20 and 25ºC the higher growth was not reflected on the growth rate and biomass productivity due to delay in the growth during the initial inoculation which resulted in lower CO_2 biofication rates. At 30C SP.PL adapted much faster and achieved the highest growth, biomass productivity and CO_2 biofixation at 15% CO_2 dosage. In the pilot plant PBR the results indicated that there is a great potential for SP.PL to be cultivated under large-scale conditions. Despite the scale-up challenges the pilot plant PBR

results showed better performance compared to the lab-scale, SP.PL achieved higher growth, biomass productivity and CO_2 biofixation. The highest growth and CO_2 biofixation was obtained at an average temperature of 25.3 and 10% CO_2 dosage. SP.PL was also tested for nutrient removal in lab-scale PBR. The nutrients removal results showed great potential for SP.PL as nutrient removal technology. SP.PL in synthetic WW was able to adapt with up to 10% CO_2 dosage, but the highest growth was achieved at 5% CO_2 injection. Nutrient removal was found to favor non-CO_2 enriched cultures since the CO_2 enriched cultures achieved lower removal%. Nutrient removal also showed variation at different temperatures [25, 30ºC], Ammonia removal was better at higher temperature while phosphorus and COD showed better removal at lower temperature. Overall SP.PL cultivated in PBR was proven to be successfully capable of CO_2 capture and Nutrients removal.

Future work:

This thesis demonstrated the ability of green algae SP.PL cultivated in lab-scale PBR and pilot plant PBR to capture carbon and remove nutrients from wastewater, there are still opportunity to expand this research in by investigating several factors as follows:

1- Testing several algal strains to study the differences in the behavior and different tolerances towards CO_2 and nutrients Concentrations
2- Investigating different flow rates and the effect on mass transfer and the adaptation process on process performance .
3- Development and testing of various gas diffusion systems to explore mass transfer limitations.
4- Investigating the Effect of culture mixing on the growth parameters.

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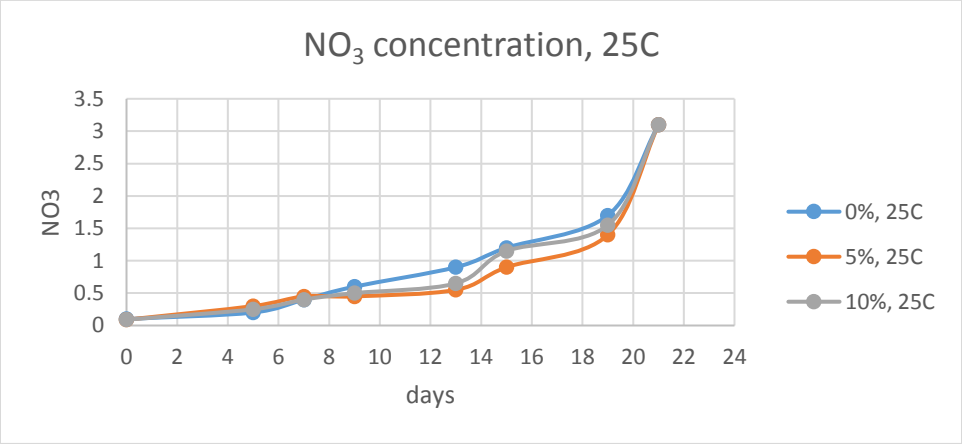
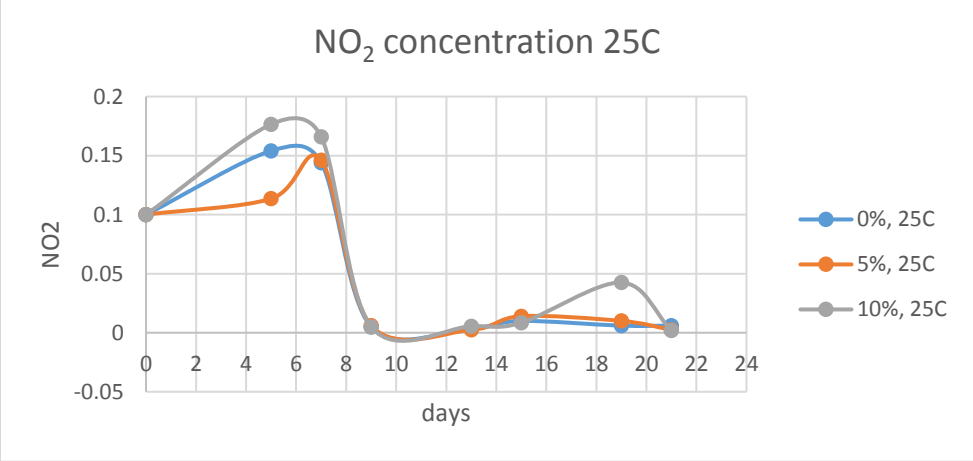
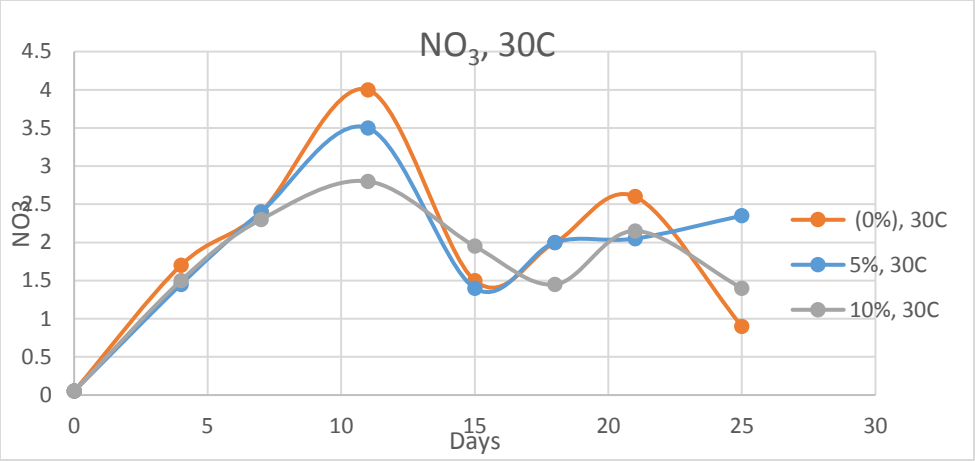
Appendices

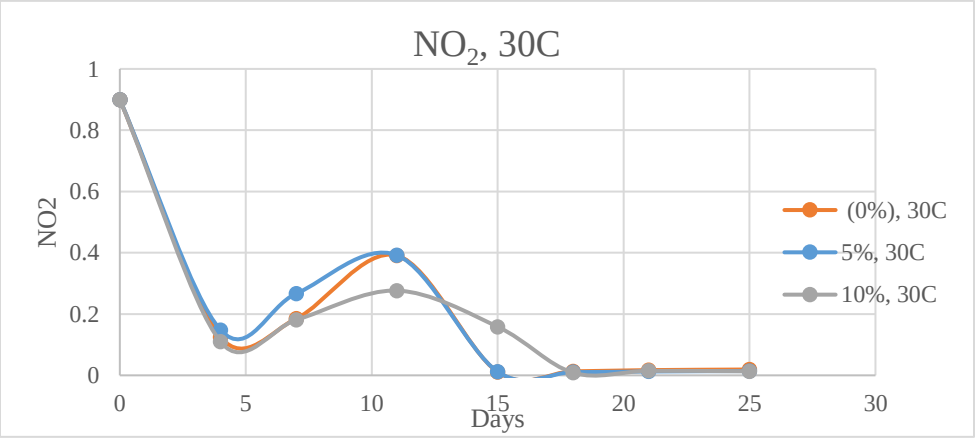
4.1 Appendix-A: nutrients removal by SP.PL:

A-1: Nitrite and Nitrate Concentration 25 and 30C:






NO3, 30C
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
NO3
0
5
10
15
20
25
30
Days
(0%), 30C
5%, 30C
10%, 30C


NO2, 30C
1
0.8
0.6
0.4
0.2
0
NO2
0
5
10
15
20
25
30
Days
(0%), 30C
5%, 30C
10%, 30C