The effects of medium salinity on the delivery of carbon dioxide to microalgae from capture solvents using a polymeric membrane system

Q. Zheng[a,b], G. J. O. Martin[b], S. E. Kentish[a*]

[a] Peter Cook Centre for CCS Research, Department of Chemical Engineering, The University of Melbourne, Parkville, Victoria 3010, Australia.

[b] Algal Processing Group, Department of Chemical Engineering, The University of Melbourne, Parkville, Victoria 3010, Australia

***Corresponding author:** sandraek@unimelb.edu.au

Key words: *Chlorella vulgaris*; *Dunaliella tertiolecta*; *Chlorella Sp.*; *Haematococcus pluvialis;* membrane; CO_2.

Abstract

Efficient provision of carbon dioxide to microalgae is one of the major challenges to cost effective large-scale cultivation. Previously we have demonstrated the effectiveness of a novel membrane system in delivering CO_2 to a marine strain of *Chlorella* sp. from CO_2-loaded solvents. In this approach, the solvent is pumped through a non-porous hollow fibre membrane immersed in a microalgae medium, allowing passive transfer of CO_2 that is utilised by the microalgae to enhance their growth, while simultaneously regenerating the solvent. In this article, we compare the growth of both fresh water and marine strains of algae using this membrane delivery system. While the fresh water medium has less pH buffering capacity and can dissolve less CO_2, it proves similarly effective in delivering CO_2 to the growing algae. Both the freshwater and marine species of *Chlorella* have slightly higher growth rates than the other species tested - *Dunaliella tertiolecta* and *Haematococcus pluvialis.* However, due to the lower osmotic pressure of the fresh water medium, more water is drawn through the membrane into the solvent than when the salt water medium is used. In conclusion, while CO_2 delivery through the membrane system is effective for both salt and fresh water media, better performance is obtained for the salt water medium.

1. Introduction

There are many factors that contribute to the commercial success of a microalgal cultivation facility. Many of these factors are related to the type of algae that are cultivated. The species must have a high growth rate, have a wide tolerance to environmental conditions, must be readily harvested and must produce biomass that is of high value, either as a nutraceutical, a biofuel or as a source of protein(Griffiths and Harrison 2009; Borowitzka 1992, 2013b). Often these objectives are conflicting. For example, small cell microalgae tend to have faster growth rates, but are more difficult to harvest and process(Borowitzka 1992, 2013b). Other factors relate to the type of cultivation facility used, including photobioreactors and raceway ponds.

The delivery of CO_2 to the facility has also been shown to be a critical factor, estimated to account for over 50% of the raw material cost in microalgal cultivation(Acién et al. 2012). In mass cultivation the most common strategy is to bubble gases into microalgae ponds or photobioreactors using a sparger (Anjos et al. 2013; Chiang et al. 2011; Zimmerman et al. 2011). However, in the process, approximately 50% to 90% of the CO_2 can escape to the atmosphere before it can be utilised (Doucha et al. 2005). To resolve this problem, microbubbles (1 - 999μm) can be produced using fluidic oscillation, ultrasound, membrane spargers or pressurized gas liquid circulation systems (Agarwal et al. 2011; Xu et al. 2011; Mortezaeikia et al. 2016). The smaller sized microbubbles have a much higher surface to volume ratio and slower rise velocity allowing them to dissolve more fully in the medium (Xu et al. 2011; Lam et al. 2012). However, there is a large pressure loss required to generate microbubbles that greatly increases the energy consumption. Further, the strong shear stresses created by microbubble generation may damage microalgae cells (Tramper et al. 1986; Fan et al. 2008). Non-porous membranes can also

be used to provide CO_2 as individual molecules in a vapour state, which cross the membrane via diffusion (Kumar et al. 2010; Kim et al. 2011). However, these systems require gaseous CO_2 to be compressed and transported through the membranes, which is highly energy intensive for large open pond or photobioreactor systems (Gao et al. 2013; Lardon et al. 2009; Stephenson et al. 2010).

In our previous work, we modified an approach originally developed by Noel et al.(Noel et al. 2012; Chance et al. 2015) to address these problems(Zheng et al. 2016; Zheng et al. 2017). In this system, CO_2-loaded solvents are passed through the inside of a non-porous polymeric membrane allowing the CO_2 stored in the solvents to cross the membrane, dissolve in the medium and become the carbon source for the microalgae (see Figure 1). This approach integrates CO_2 capture via chemical absorption, membrane separation and microalgae cultivation technologies, and eliminates both the energy consumption of gas compression and transportation, and the energy penalty for regeneration of the capture solvent. The system has been shown to be effective for a range of CO_2 capture solvents including potassium carbonate (K_2CO_3), monoethanolamine (MEA) and potassium glycinate (PG) (Zheng et al. 2017). However, to date the system has only been tested on a marine strain of *Chlorella* sp., and it is not clear how the performance will be affected by the low salinity media required for fresh water microalgae.

In this article the performance of the membrane system is compared between four algal species, two freshwater and two salt water (marine) algae. The selected freshwater microalgae are *Chlorella vulgaris*, a species with health food applications and *Haematococcus pluvialis,* a source of the natural pigment and antioxidant, astaxanthin

($C_{40}H_{52}O_4$, 3,3′-dihydroxy-β,β′-carotene-4,4′-dione). The chosen marine microalgae are *Dunaliella tertiolecta*, a species that can tolerate high salinity(Kim et al. 2013), and *Chlorella sp*. which is again a general health food.

The aim is firstly to confirm the relative growth rates of each species under these identical environmental conditions; and secondly to confirm that the CO_2 delivery mechanism is equally effective in both freshwater and marine systems. Ultimately, this data is necessary to evaluate the commercial potential of different species using this technology.

2. Materials and methods

2.1 Materials

The CO_2 absorbing solvents used in this study were potassium carbonate (K_2CO_3), monoethanolamine (MEA) and potassium glycinate (PG). All were prepared to a loading of 0.5 mol CO_2 per mol of solvent, which is the maximum possible loading for the latter two solvents.

20 wt% K_2CO_3 of 0.5 CO_2 loading was prepared by addition of 114.8 g K_2CO_3 (Senator Chemicals, 99.7%) and 166.4 g $KHCO_3$ (Univar, 98%) to 903.6 g purified water (Millipore Elix)(Zheng et al. 2016). The CO_2 loading was defined as the moles of all CO_2 carrying species per mole of solvent. The CO_2 loading of K_2CO_3 solvent was calculated as:

$$\text{CO}_2 \text{ loading in } \text{K}_2\text{CO}_3 = \frac{[\text{HCO}_3^-]}{[\text{K}^+]} \qquad (1)$$

Both 1M and 2M PG (11 and 22 wt%) were prepared by adding equimolar amounts of potassium hydroxide (Chem-supply, 99%) to glycine (Chem-supply, 99%) and dissolving into purified water (Millipore Elix) (Guo et al. 2013). CO_2-loaded MEA and PG were prepared by bubbling pure CO_2 gas into the solutions for 30 min to saturate with CO_2. The CO_2 loading was measured by coulometry (CM5015 Coulometer, UIC Inc., USA) and calculated as:

$$CO_2 \text{ loading in MEA} = \frac{[CO_2] + [HCO_3^-] + [CO_3^{2-}] + [HOCH_2CH_2NHCOO^-]}{[HOCH_2CH_2NH_2] + [HOCH_2CH_2NH_3^+] + [HOCH_2CH_2NHCOO^-]} \quad (2)$$

$$CO_2 \text{ loading in PG} = \frac{[CO_2] + [HCO_3^-] + [CO_3^{2-}] + [^-OOCCH_2NHCOO^-]}{[^-OOCCH_2NH_2] + [^-OOCCCH_2NH_3^+] + [^-OOCCCH_2NHCOO^-]} \quad (3)$$

Composite membranes (Airrane, Korea) containing a porous polysulfone support layer coated with a thin, non-porous polydimethylsiloxane (PDMS) layer were utilized in this study as previously described(Zheng et al. 2016).

A modified-F (MF) salt water medium was prepared by adding 1.0 mL of each of five stock solutions(Olmstead et al. 2013) and 30g of ocean salt (Ocean Fish, Prodac International, Italy) into 1 litre purified water, then filtering through a 0.22 μm Millipore filter. The concentrations of the major ions in the resulting medium are presented in Table 1, as measured using inductively coupled plasma optical emission spectrometry and Ion Chromatography. Note that while the MF medium was prepared with 30 g of ocean salt per litre, the final salt concentration was of the order of 25 g L^{-1}. This lower concentration probably results from the loss of some undissolved salts during filtration of the solution.

A freshwater MLA medium was prepared by adding 25mL of nutrient solutions and 1mL of a $CaCl_2 \cdot 2H_2O$ solution into purified water to reach a volume of one Litre, then filtering through a 0.22 μm Millipore filter(Bolch and Blackburn 1996). As this research studied the supply of CO_2 from CO_2-loaded solvents, addition of $NaHCO_3$ was excluded from the standard medium preparation.

Table.1 Composition of the salt water MF and fresh water MLA media*

	Concentration (mg L^{-1} MF)	Concentration (mg L^{-1} MLA)
Na^+	8510 ± 30	49 ± 0.1
Mg^{2+}	860 ± 10	4.6 ±0.2
Ca^{2+}	280 ± 30	7.6 ± 0.7
K^+	510 ± 50	16.1 ± 0.1
phosphorus	3.7 ±0. 8	7.2 ± 0.1
boron	3.2 ±0.3	0.4 ± 0.1
DIC	2.5 ± 0.2	1.0 ± 0.1
pH	7.8	7.1

* Error margins represent the difference between duplicate samples of medium.

2.2 Microalgal strains and cultivation

The freshwater *Chlorella vulgaris* was obtained from CSIRO, Australia, while the fresh water *Haematococcus pluvialis* was isolated from a rooftop in the Parkville campus, VIC, Australia. Marine species *Dunaliella tertiolecta* was isolated from Port Phillip Bay, VIC, Australia, while *Chlorella* sp., which was isolated from the Cooper Creek at Innamincka, SA, Australia(Olmstead et al. 2013).

The microalgae were cultivated in 500-mL Erlenmeyer flasks filled with 400 mL medium and agitated at 120 rpm on an orbital shaker (SS70, Chiltern Scientific, Australia). The cultures were grown at ambient temperature (25 ±3 ^{o}C) under an evenly distributed light intensity of approximately 130 μmol m^{-2} s^{-1} (Zheng et al. 2016). This light intensity was determined using a portable light meter (Dick Smith Electronics, Australia). To reduce water evaporation and bacterial contamination flask openings were covered with a vented plastic film. Hollow fibre PDMS membranes were immersed in the microalgal medium as described previously (Zheng et al. 2016). The CO_2-loaded solvents were passed through the internal channels of the membrane at a flowrate of 0.63 L h^{-1} using peristaltic pumps. All experiments were conducted in duplicate.

2.3 Analyses

Ten mL samples of microalgae broth were taken daily. The optical density of these samples was measured at a wavelength of 750 nm (Cary 3E UV-Vis, Agilent Technologies, Australia) and converted to dry weight using a previously established calibration curve that was unique to each species. The total carbon and dissolved inorganic carbon (DIC) in the samples were measured using a Total Organic Carbon Analyser (TOC-VCSH, Shimadzu, Japan). Dry weight was measured with a 20 mL sample taken at the end of cultivation. These samples were filtered through glass microfiber filters (Whatman GF/C 47mm) and washed once with 20 mL deionized water and dried for 16h at 105 ^{o}C (Chiu et al. 2009). Water permeation from the media into the solvent was determined by comparing the initial and final volumes of both the solvents and media. Taking into account the sample volumes removed, the loss of medium volume was comparable to the

gain in solvent volume. The water permeation rate was calculated by dividing this change in volume by the inoculation days.

The concentrations of metals (K, Na, Ca, Mg) and those of inorganic elements (boron, phosphorus) in media were determined using inductively coupled plasma optical emission spectrometry (ICP-OES 720 ES, Varian, USA) as previously described (Zheng et al. 2016).

The potassium carbonate and potassium bicarbonate concentration of the K_2CO_3 solvent was determined by titration against 0.4 mol L^{-1} sulfuric acid (905 Titrando autotitrator, Metrohm, Switzerland). A Total Inorganic Carbon Analyser (CM140, UIC Inc., USA) was used to monitor the CO_2 concentration of the MEA and PG solvents. This automated device initially purges the sampling unit of atmospheric carbon, then acidifies the sample to evolve CO_2, passes it through a scrubber to remove interferences and then uses coulometric titration to evaluate the CO_2 concentration.

The method developed by Olmstead et al.(Olmstead et al. 2013) was used to determine the percentage of lipids in the dry biomass. Briefly, 1.2 ml of concentrated biomass was mixed with 4.5 mL methanol and 3 mL chloroform. After centrifugation, the bottom chloroform phase containing the extracted lipid was collected. The remaining biomass was re-suspended in water and mixed with more methanol and chloroform as above. This process was repeated twice more.The final chloroform phase was dried by nitrogen stripping at 40 ℃. The remaining mass was considered to represent the recovered lipids.

The osmotic pressure associated with each solvent and algal medium was determined using the software package Aspen Plus™ Version 9.0 (Aspen Technology, Inc. USA).

3. Results and discussion

3.1 Carbon concentrations in the media

When carbon dioxide ($CO_{2(g)}$) is dissolved in water, it is first hydrated and then reacts with H^+ ions present in solution until equilibria is reached between four inorganic carbon species: carbon dioxide ($CO_{2(aq)}$), carbonic acid (H_2CO_3), bicarbonate ion (HCO_3^-) and carbonate ion (CO_3^{2-}). The proportion of bicarbonate ion (HCO_3^-) and carbonate ion (CO_3^{2-}) depends primarily upon the pH, with bicarbonate ions dominating at moderate pH and carbonate ions at higher pH. However, the salt water medium has high concentrations of other ions such as Na^+, Cl^- and Mg^{2+}, with an overall ionic strength of approximately 0.5 mol kg^{-1}. This causes a 'salting out' effect, reducing the CO_2 solubility (Henry's Law coefficient) in the salt water medium. Further, the equilibrium concentrations of bicarbonate and carbonate anions increase due to reductions in the activity coefficients of these ions. Based on the equation introduced by Weiss in 1974 (Weiss 1974) and dissociation constants determined by Roy et al.(Roy et al. 1993), the dissolved inorganic carbon concentrations (DIC) were calculated for seawater and pure water at pH 7, assuming an atmospheric CO_2 concentration of 400 ppm. The results, presented in Table 2, show that seawater has a higher DIC concentration (2.0 mg L^{-1}) than pure water (0.9 mg L^{-1}). In comparison, the measured DIC concentration of the initial salt water medium was 2.5 mg L^{-1} and of the initial freshwater media was 1.0 mg L^{-1} (Table 1).

Table 2 Equilibrium dissolved inorganic Carbon (DIC) concentrations in pure water and seawater at pH 7, 25°C and 400 ppm CO_2 in the atmosphere estimated based on the coefficients determined from Weiss et al. (Weiss 1974) and Roy et al. (Roy et al. 1993)

	CO_2(mg C L^{-1})	HCO_3^-(mg C L^{-1})	CO_3^{2-}(mg C L^{-1})	DIC(mg L^{-1})
Pure water	0.16	0.73	0.0003	0.9
Seawater	0.13	1.89	0.02	2.0

3.2 pH Effects

As mentioned above, for a given salinity the pH of the medium is a direct indication of the carbonate and bicarbonate concentrations within this solution(Snoeyink and Jenkins 1980). In both fresh and salt water media, the pH usually dropped sharply in the first half day due to the high rate of CO_2 delivery, which exceeded the demands of the low-density algae cultures that were still in the lag-phase (Figure 2). In the following days as the microalgae began to grow, the rate of CO_2 consumption increased such that the pH increased to reach reasonably stable values. With only atmospheric CO_2 (control), the pH of the *Chlorella vulgaris* culture grown in a fresh water medium increased from 7.5 to 10.5 in 14 days (Figure 2a), while that in freshwater *Haematococcus pluvialis* reached pH 11 (Figure 2b). However, the pH of *Dunaliella tertiolecta* cultures grown in the salt water media increased from 7.5 to only 9 (Figure 2c), which is consistent with our previous studies using a marine strain of *Chlorella* sp.(Zheng et al. 2017). The high concentrations of buffering ionic species present in the salt water medium (such as HCO_3^{2-}, $B(OH)_3$, HPO_4^{2-}) contribute protons to the medium as the pH rises, thus reducing the extent of this increase.

3.2 Microalgal productivity

Typical growth patterns of the four species are shown in Figure 3, for the systems using potassium glycinate (PG) and MEA as solvent. Both freshwater and marine *Chlorella* species were comparably productive in PG. It is noteworthy that these growth rates were also identical whether 1M or 2M potassium glycinate was used as the source of carbon dioxide for the marine *Chlorella Sp.* This implies that at these solvent concentrations, 1M potassium glycinate was sufficient to supply the carbon dioxide needed for growth. The optimum pH for biomass growth is reported as 6.5-7.5(Sharif et al. 2015), which is consistent with the average value of 7.2 recorded during the growth phase for the 2M case. However, the pH for the 1M PG growth was higher at 8.0 during the growth phase due to the lower CO_2 supply. This suggests that while growth was not affected in this case within experimental error, a 1M solution may provide sub-optimal growth in other circumstances.

For this solvent, lower productivity was observed for *Dunaliella tertiolecta,* with the lowest rate for *Haematococcus pluvialis.* We believe that the poorer performance of *Haematococcus pluvialis* in the experiments using PG (Figure 3a) relative to MEA (Figure 3b) relates to an oversupply of CO_2 to this freshwater species, as indicated by a slightly lower pH at Day 2 (Figure 2b), which led to an extended lag phase.(Dos Santos and Lombardi 2017) observed a maximum specific growth rate for this species at pH 6.3, which would suggest that the pH observed at Day 2 should not have been inhibitive. However, it is probable that the pH was even lower at Day 1 (as observed in Figures 2a and 2c). (Sarada et al. 2002) observed no growth of this species at pH 5.0, and it is possible that the pH fell to this level during Day 1, given the lack of buffering in this fresh water system.

The slightly lower productivity for the marine *Chlorella sp.* when using monoethanolamine (MEA) (Figure 3B) was noted in our previous paper(Zheng et al. 2017) to result from a small permeation of the neutral MEA into the algal medium having a toxic effect on this species. It is interesting that this permeation of MEA has had less effect on the freshwater species (Figure 3b).

The impact of the three solvents used to deliver the CO_2 is further provided in Figure 4. For the marine species *Dunaliella tertiolecta* there was little difference in growth performance between these delivery methods, with comparable values of the average and maximum volumetric productivities. For freshwater *Chlorella vulgaris*, the volumetric productivity and lipid yield was better for the PG and MEA solvents relative to the K_2CO_3 solvent. The pH curve for this species (see Figure 2) suggests that in this case the K_2CO_3 solvent was less effective in delivering carbon dioxide than the other solvents, as the pH did not fall as far in the lag phase as with the other solvents. As described above, for *Haematococcus pluvialis*, the performance in the PG solvent suffered because too much CO_2 was delivered.

While the two *Chlorella* species had the highest growth rates, there is greatest economic potential from cultivation of *Haematococcus pluvialis* with potential sales of up to \$210/kg biomass versus \$36/kg biomass for *Chlorella* sp. (see Table 3). *Dunaliella tertiolecta* had comparable growth rates to *Haematococcus pluvialis* and is also economically attractive with potential sales of up to \$260/kg biomass (Table 3). It should be noted that these prices are the maximum and the actual sales prices may be lower, as shown in Table 3.

Table 3 – A comparison of the potential sales revenue that can be generated from the different species of Algae tested in this work.

	Yield (g/kg)	Sales Price (US$/kg)	Price per kg biomass	
Astaxanthin (*Haematococcus pluvialis)*	15-30	2500-7000	$38 - $210	(Kim et al. 2016; Lorenz and Cysewski 2000) (García Prieto et al. 2017) (Panis and Carreon 2016)
Chlorella sp.			36	(Kim et al. 2016)
Dunaliella tertiolecta	87	300 - 3000	$26-$260	(Thomassen et al. 2016) (Borowitzka 2013a; Richmond and Hu 2013))

The percentage lipid by mass appears to be independent of the solvent used (Figure 5). The lipids recovered from *Chlorella vulgaris* were generally lower than previously reported in the literature, while that for *Dunaliella tertiolecta* was higher(Griffiths and Harrison 2009).

3.3 Osmotic pressure

During microalgae cultivation water passes from the medium side to the chemical solvent side of the membrane in response to the osmotic pressure gradient. As shown in Figure 6A, the water permeation rate into the solvent was lower for the salt water (MF) medium than from the freshwater (MLA) medium, due to its higher ionic strength (around 0.5 mol

kg $^{-1}$) reducing the osmotic pressure driving force. 30 wt% MEA had the highest osmotic pressure among the three solvents (Figure 6B). The trend in the osmotic pressure difference between these chemical solvents and the growth media was consistent with the water permeation rate through the membranes.

Conclusions

Different microalgae species prefer to grow in water of different salinities, with freshwater and salt water (seawater), two main microalgae cultivation environments of potential commercial significance. The results presented here show that when operated with a salt water medium there is improved buffering capacity. This can reduce the extent of pH swings, which can limit growth of sensitive species such as *Haematococcus pluvialis*. The salt water medium also contains more dissolved inorganic carbon, increasing the local availability of carbon as an algal food source. Operating the membrane system in a marine environment also reduces the flow of water from the medium into the solvent, due to the higher osmotic pressure. This reduces the rate of dilution of the solvent, which would allow the solvent to be circulated more extensively.

Aside from the issue with *Haematococcus pluvialis*, the differences between the two media, had little impact upon microalgal cultivation. Fresh water *Haematococcus pluvialis* and marine *Dunaliella tertiolecta* had the lowest growth rates on average, but these species are of highest potential economic potential.

The next steps in this research are both to increase the scale of the operation and to develop a mechanism to control the flow of solvent through the hollow fibres to provide only the CO_2 required by the algae, rather than a constant amount.

Acknowledgements

Specialist gas infrastructure and analytical equipment were funded by the Australian Government Education Investment Fund and this support is gratefully acknowledged. The authors also acknowledge The University of Melbourne for providing a Melbourne International Engagement Award scholarship for Ms. Zheng.

References

Acién F, Fernández J, Magán J, Molina E (2012) Production cost of a real microalgae production plant and strategies to reduce it. Biotechnology advances 30 (6):1344-1353

Agarwal A, Ng WJ, Liu Y (2011) Principle and applications of microbubble and nanobubble technology for water treatment. Chemosphere 84 (9):1175-1180

Anjos M, Fernandes BD, Vicente AA, Teixeira JA, Dragone G (2013) Optimization of CO2 bio-mitigation by Chlorella vulgaris. Bioresource Technol 139:149-154. doi:DOI 10.1016/j.biortech.2013.04.032

Bolch CJ, Blackburn SI (1996) Isolation and purification of Australian isolates of the toxic cyanobacteriumMicrocystis aeruginosa Kütz. Journal of Applied Phycology 8 (1):5-13

Borowitzka MA (1992) Algal biotechnology products and processes — matching science and economics. Journal of Applied Phycology 4 (3):267-279. doi:10.1007/BF02161212

Borowitzka MA (2013a) High-value products from microalgae—their development and commercialisation. Journal of Applied Phycology 25 (3):743-756. doi:10.1007/s10811-013-9983-9

Borowitzka MA (2013b) Species and Strain Selection. In: Borowitzka MA, Moheimani NR (eds) Algae for Biofuels and Energy. Springer Netherlands, Dordrecht, pp 77-89. doi:10.1007/978-94-007-5479-9_4

Chance RR, Koros WJ, McCool BA, Noel JD (2015) Water/carbonate stripping for CO2 capture adsorber regeneration and CO2 delivery to photoautotrophs United States Patent US9101093B2.

Chiang CL, Lee CM, Chen PC (2011) Utilization of the cyanobacteria Anabaena sp CH1 in biological carbon dioxide mitigation processes. Bioresource Technol 102 (9):5400-5405. doi:DOI 10.1016/j.biortech.2010.10.089

Chiu SY, Kao CY, Tsai MT, Ong SC, Chen CH, Lin CS (2009) Lipid accumulation and CO 2 utilization of Nannochloropsis oculata in response to CO 2 aeration. Bioresource Technol 100 (2):833-838

Dos Santos AC, Lombardi AT (2017) Growth, photosynthesis and biochemical composition of Haematococcus pluvialis at various pH. Journal of Algal Biomass Utilisation 8 (1):1-15

Doucha J, Straka F, Lívanský K (2005) Utilization of flue gas for cultivation of microalgae Chlorella sp.) in an outdoor open thin-layer photobioreactor. Journal of Applied Phycology 17 (5):403-412

Fan LH, Zhang YT, Zhang L, Chen HL (2008) Evaluation of a membrane-sparged helical tubular photobioreactor for carbon dioxide biofixation by Chlorella vulgaris. Journal of Membrane Science 325 (1):336-345. doi:DOI 10.1016/j.memsci.2008.07.044

Gao X, Yu Y, Wu H (2013) Life cycle energy and carbon footprints of microalgal biodiesel production in Western Australia: a comparison of byproducts utilization strategies. ACS Sustainable Chemistry & Engineering 1 (11):1371-1380

García Prieto CV, Ramos FD, Estrada V, Villar MA, Diaz MS (2017) Optimization of an integrated algae-based biorefinery for the production of biodiesel, astaxanthin and PHB. Energy 139:1159-1172. doi:https://doi.org/10.1016/j.energy.2017.08.036

Griffiths MJ, Harrison STL (2009) Lipid productivity as a key characteristic for choosing algal species for biodiesel production. Journal of Applied Phycology 21 (5):493-507. doi:10.1007/s10811-008-9392-7

Guo D, Thee H, Tan CY, Chen J, Fei W, Kentish S, Stevens GW, da Silva G (2013) Amino acids as carbon capture solvents: chemical kinetics and mechanism of the glycine+ CO2 reaction. Energy & Fuels 27 (7):3898-3904

Kim D-Y, Vijayan D, Praveenkumar R, Han J-I, Lee K, Park J-Y, Chang W-S, Lee J-S, Oh Y-K (2016) Cell-wall disruption and lipid/astaxanthin extraction from microalgae: Chlorella and Haematococcus. Bioresource Technol 199:300-310. doi:https://doi.org/10.1016/j.biortech.2015.08.107

Kim HW, Marcus AK, Shin JH, Rittmann BE (2011) Advanced Control for Photoautotrophic Growth and CO2-Utilization Efficiency Using a Membrane Carbonation Photobioreactor (MCPBR). Environmental Science & Technology 45 (11):5032-5038

Kim S-H, Liu K-H, Lee S-Y, Hong S-J, Cho B-K, Lee H, Lee C-G, Choi H-K (2013) Effects of Light Intensity and Nitrogen Starvation on Glycerolipid, Glycerophospholipid, and Carotenoid Composition in Dunaliella tertiolecta Culture. PLOS ONE 8 (9):e72415. doi:10.1371/journal.pone.0072415

Kumar A, Yuan X, Sahu AK, Ergas SJ, Van Langenhove H, Dewulf J (2010) A hollow fiber membrane photo-bioreactor for CO2 sequestration from combustion gas coupled with wastewater treatment: A process engineering approach. J Chem Technol Biot 85 (3):387-394

Lam MK, Lee KT, Mohamed AR (2012) Current status and challenges on microalgae-based carbon capture. International Journal of Greenhouse Gas Control 10:456-469. doi:DOI 10.1016/j.ijggc.2012.07.010

Lardon L, Helias A, Sialve B, Steyer J-P, Bernard O (2009) Life-cycle assessment of biodiesel production from microalgae. Environmental science & technology 43 (17):6475-6481

Lorenz RT, Cysewski GR (2000) Commercial potential for Haematococcus microalgae as a natural source of astaxanthin. Trends in Biotechnology 18 (4):160-167. doi:https://doi.org/10.1016/S0167-7799(00)01433-5

Mortezaeikia V, Yegani R, Tavakoli O (2016) Membrane-sparger vs. membrane contactor as a photobioreactors for carbon dioxide biofixation of Synechococcus elongatus in batch and semi-continuous mode. Journal of CO2 Utilization 16:23-31

Noel JD, Koros WJ, McCool BA, Chance RR (2012) Membrane-Mediated Delivery of Carbon Dioxide for Consumption by Photoautotrophs: Eliminating Thermal Regeneration in Carbon Capture. Industrial & Engineering Chemistry Research 51 (12):4673-4681

Olmstead IL, Hill DR, Dias DA, Jayasinghe NS, Callahan DL, Kentish SE, Scales PJ, Martin GJ (2013) A quantitative analysis of microalgal lipids for optimization of biodiesel and omega‐3 production. Biotechnology and bioengineering 110 (8):2096-2104

Panis G, Carreon JR (2016) Commercial astaxanthin production derived by green alga Haematococcus pluvialis: A microalgae process model and a techno-economic assessment all through production line. Algal Research 18:175-190. doi:https://doi.org/10.1016/j.algal.2016.06.007

Richmond A, Hu Q (2013) Handbook of Microalgal Culture : Applied Phycology and Biotechnology. John Wiley & Sons, Incorporated, Hoboken, UNITED KINGDOM

Roy RN, Roy LN, Vogel KM, Porter-Moore C, Pearson T, Good CE, Millero FJ, Campbell DM (1993) The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45 C. Marine Chemistry 44 (2-4):249-267

Sarada R, Bhattacharya S, Ravishankar GA (2002) Optimization of culture conditions for growth of the green alga Haematococcus pluvialis. World Journal of Microbiology and Biotechnology 18:517-521

Sharif N, Munir N, Saleem F, Aslam F, Naz S (2015) Mass cultivation of various algal species and their evaluation as a potential candidate for lipid production. Natural Product Research 29 (20):1938-1941. doi:10.1080/14786419.2015.1010163

Snoeyink VL, Jenkins D (1980) Water chemistry. John Wiley,

Stephenson AL, Kazamia E, Dennis JS, Howe CJ, Scott SA, Smith AG (2010) Life-cycle assessment of potential algal biodiesel production in the United Kingdom: a comparison of raceways and air-lift tubular bioreactors. Energy & Fuels 24 (7):4062-4077

Thomassen G, Egiguren Vila U, Van Dael M, Lemmens B, Van Passel S (2016) A techno-economic assessment of an algal-based biorefinery. Clean Technologies and Environmental Policy 18 (6):1849-1862. doi:10.1007/s10098-016-1159-2

Tramper J, Williams J, Joustra D, Vlak J (1986) Shear sensitivity of insect cells in suspension. Enzyme and microbial technology 8 (1):33-36

Weiss RF (1974) Carbon dioxide in water and seawater: the solubility of a non-ideal gas. Marine chemistry 2 (3):203-215

Xu Q, Nakajima M, Liu Z, Shiina T (2011) Biosurfactants for microbubble preparation and application. International journal of molecular sciences 12 (1):462-475

Zheng Q, Martin GJ, Kentish SE (2016) Energy efficient transfer of carbon dioxide from flue gases to microalgal systems. Energy & Environmental Science

Zheng Q, Martin GJ, Wu Y, Kentish SE (2017) The use of monoethanolamine and potassium glycinate solvents for CO2 delivery to microalgae through a polymeric membrane system, under review. Biochemical Engineering Journal 128:126-133

Zimmerman WB, Tesar V, Bandulasena HCH (2011) Towards energy efficient nanobubble generation with fluidic oscillation. Curr Opin Colloid In 16 (4):350-356

Figure Captions

Figure 1 – A schematic of the solvent process for delivery of carbon dioxide to algal media.

Figure 2 - The pH of fresh water *Chlorella vulgaris* (a) and *Haematococcus pluvialis* (b), and marine *Dunaliella tertiolecta* (c) cultures provided CO_2 by membrane delivery from K_2CO_3, MEA and PG of 0.5 CO_2 loading or by atmospheric diffusion only (the control). The duplicate points represent duplicate cultures grown over the same time period.

Figure 3 - Dry biomass weight of cultures provided CO_2 by membrane delivery from PG of 0.5 CO_2 loading and concentration both 1M and 2M (a) and MEA at a CO_2 loading of 0.5 (b). The duplicate points represent duplicate cultures grown over the same time period.

Figure 4 – Average and maximum volumetric productivity (g L^{-1} d^{-1}) for the four algal strains provided with CO_2 from different solvents. The error bars here are an estimate of the variability between cultures grown over different time periods and hence possibly at slightly different temperatures.

Figure 5 - Percentage lipids in the final dried biomass after a fortnight of growth. The error bars represent duplicate cultures grown over the same time period.

Figure 6 - Water passage across the membrane into the solvent side (A), and the osmotic pressure of the solvents and growth media (B). The error bars represent duplicate cultures grown over the same time period.

Figure 1

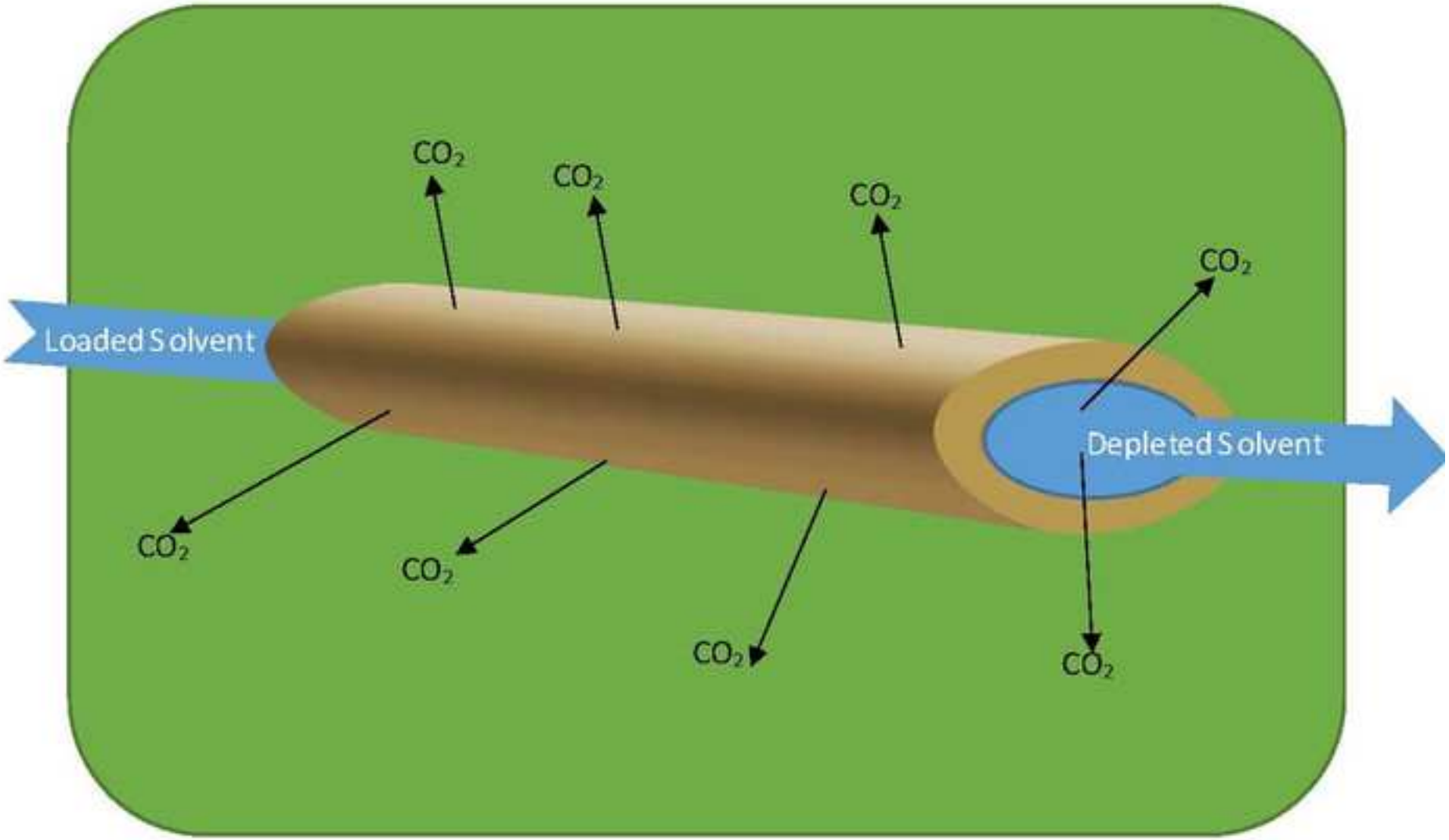

CO2
CO2
CO2
CO2
Loaded Solvent
Depleted Solvent
CO2
CO2
CO2
CO2

Figure 2a

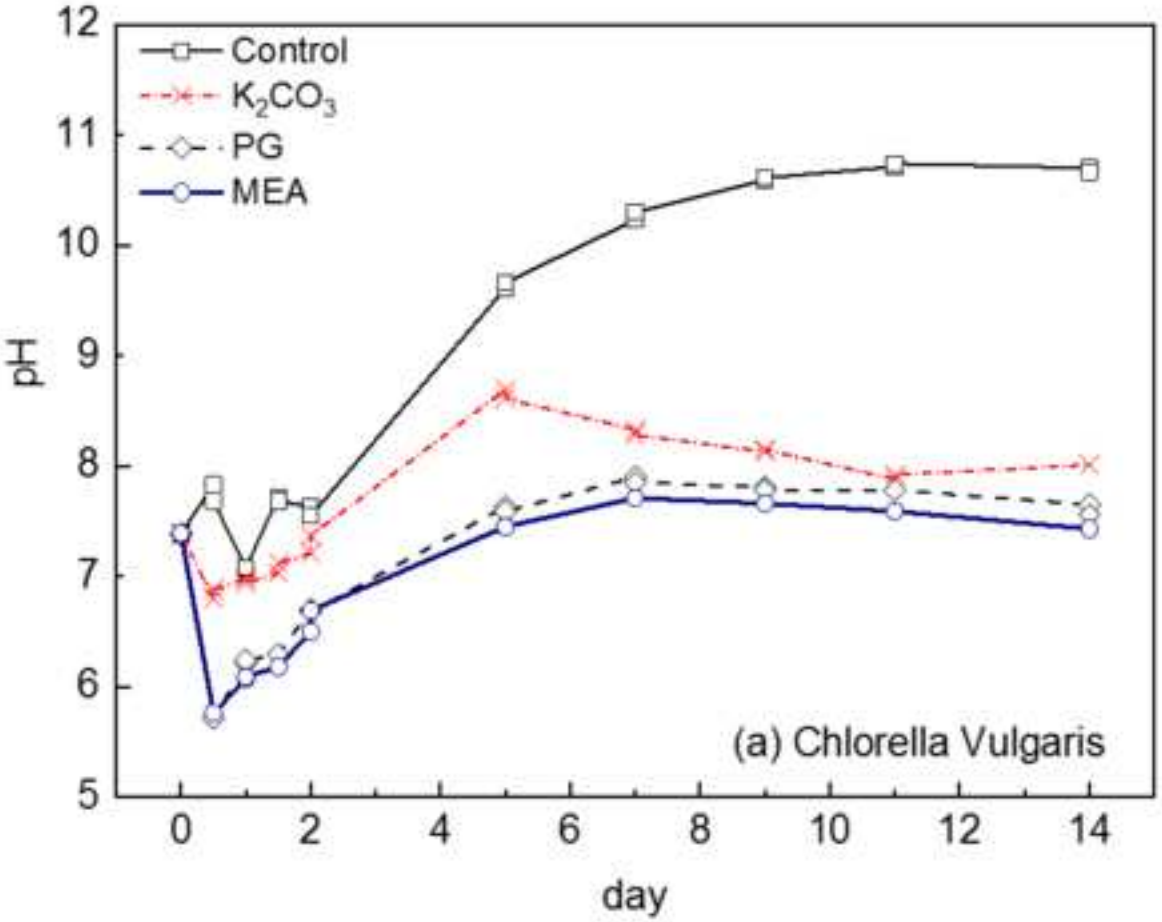

Control
K_2CO_3
PG
MEA
pH
day
(a) Chlorella Vulgaris
12
11
10
9
8
7
6
5
0
2
4
6
8
10
12
14

Figure 2b

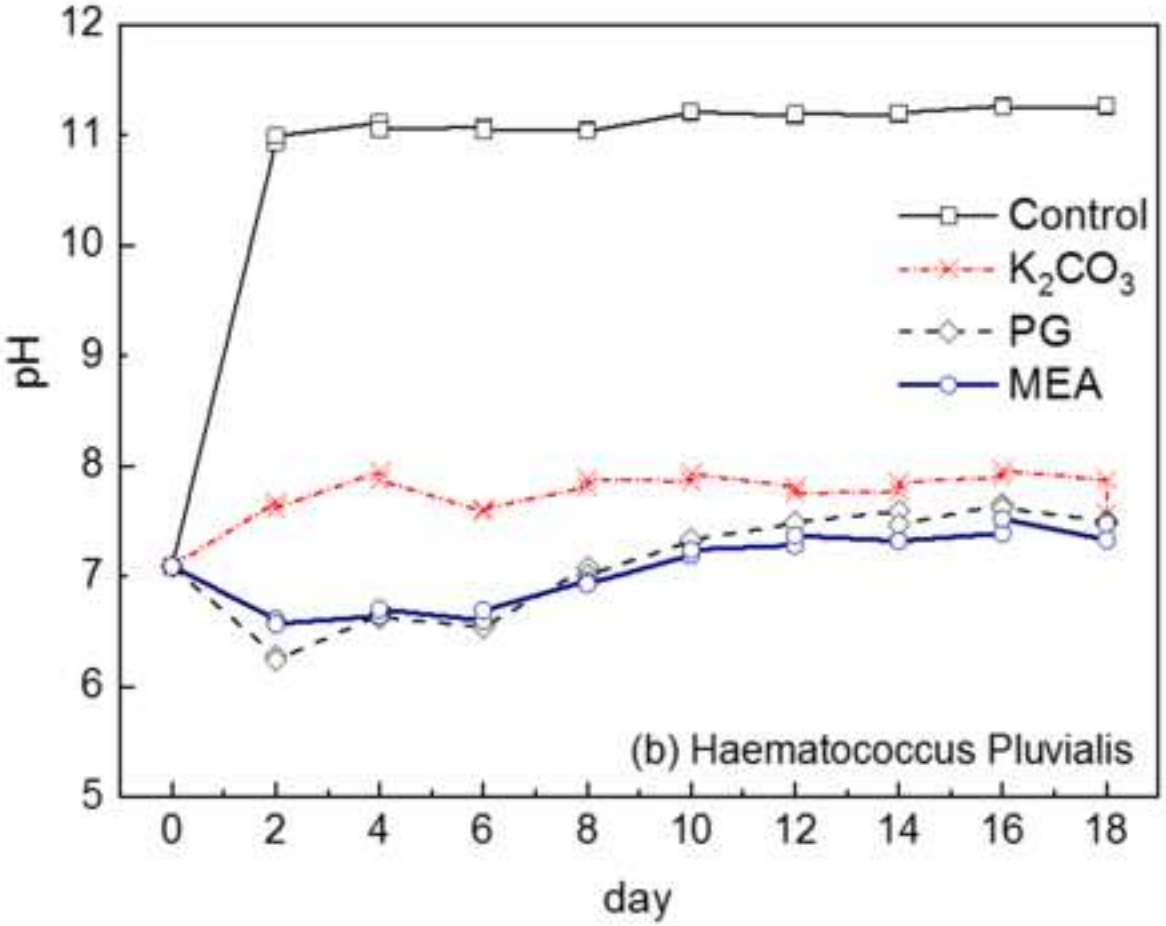

12
11
10
9
8
7
6
5
pH
0
2
4
6
8
10
12
14
16
18
day
Control
K_2CO_3
PG
MEA
(b) Haematococcus Pluvialis

Figure 2c

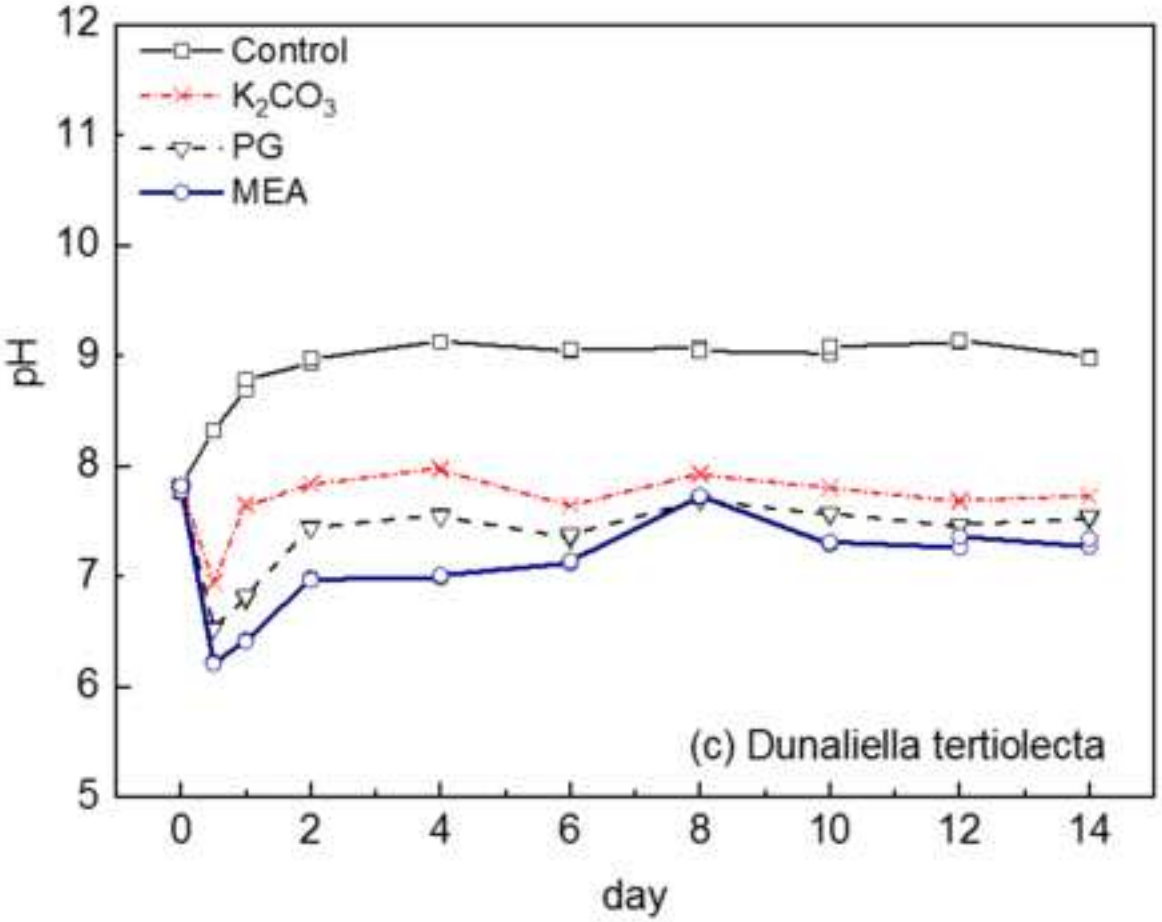

Control
K2CO3
PG
MEA
pH
day
(c) Dunaliella tertiolecta
12
11
10
9
8
7
6
5
0
2
4
6
8
10
12
14

Figure 3a

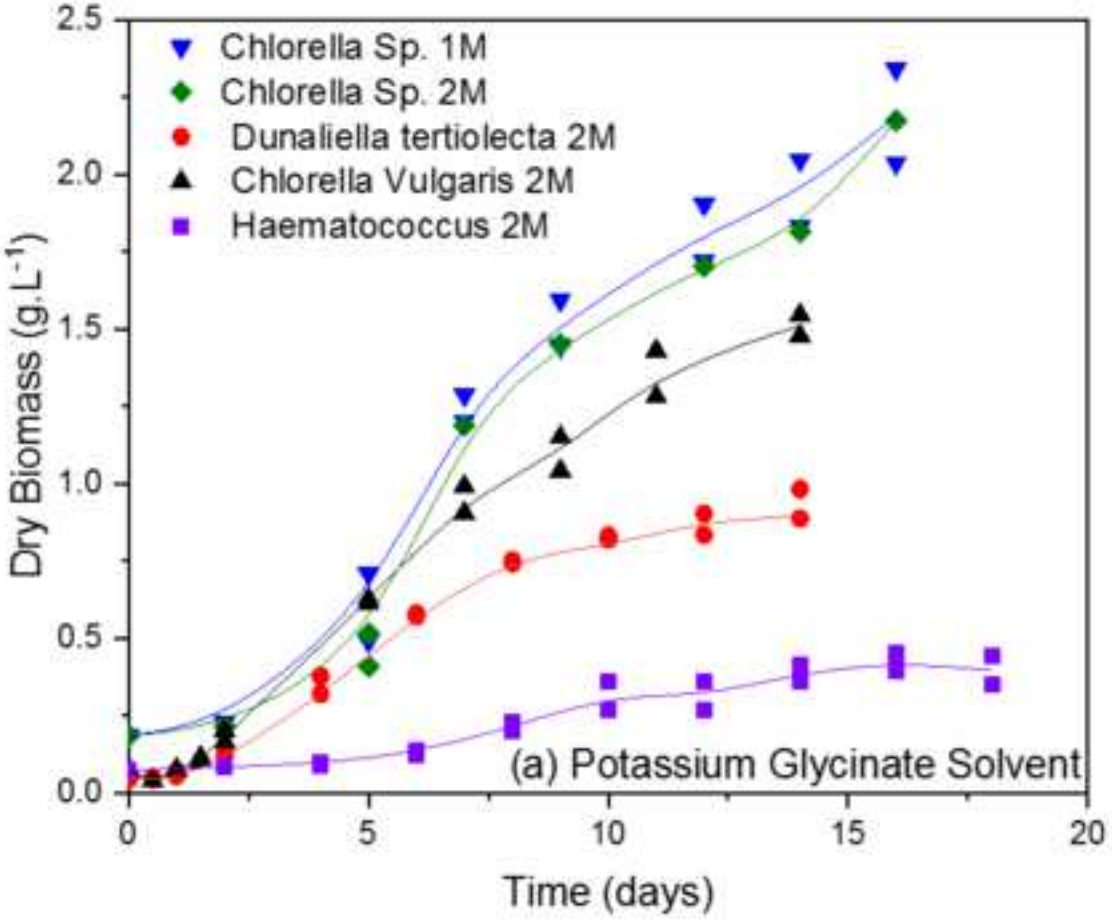

Chlorella Sp. 1M
Chlorella Sp. 2M
Dunaliella tertiolecta 2M
Chlorella Vulgaris 2M
Haematococcus 2M
(a) Potassium Glycinate Solvent
Dry Biomass (g.L-1)
Time (days)
0.0
0.5
1.0
1.5
2.0
2.5
0
5
10
15
20

Figure 3b

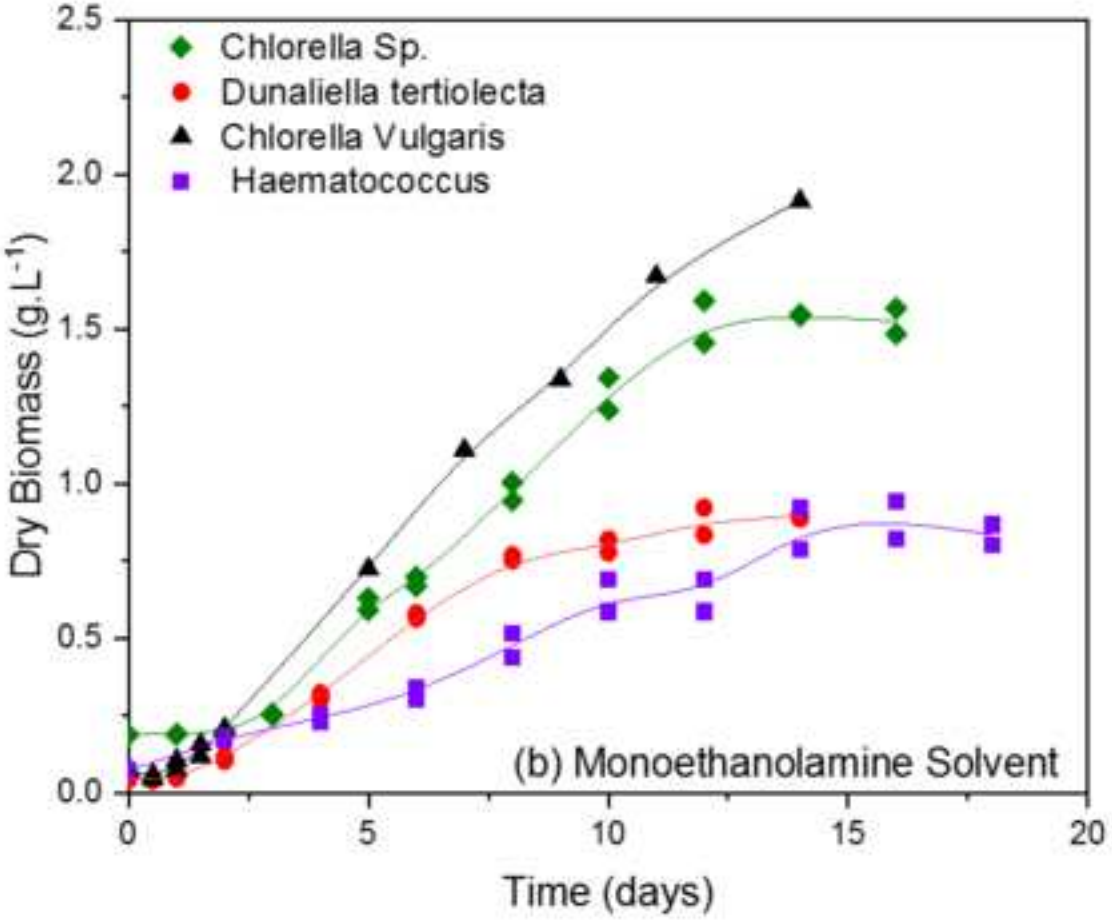

Chlorella Sp.
Dunaliella tertiolecta
Chlorella Vulgaris
Haematococcus
(b) Monoethanolamine Solvent
Dry Biomass (g.L-1)
Time (days)
0.0
0.5
1.0
1.5
2.0
2.5
0
5
10
15
20

Figure 4

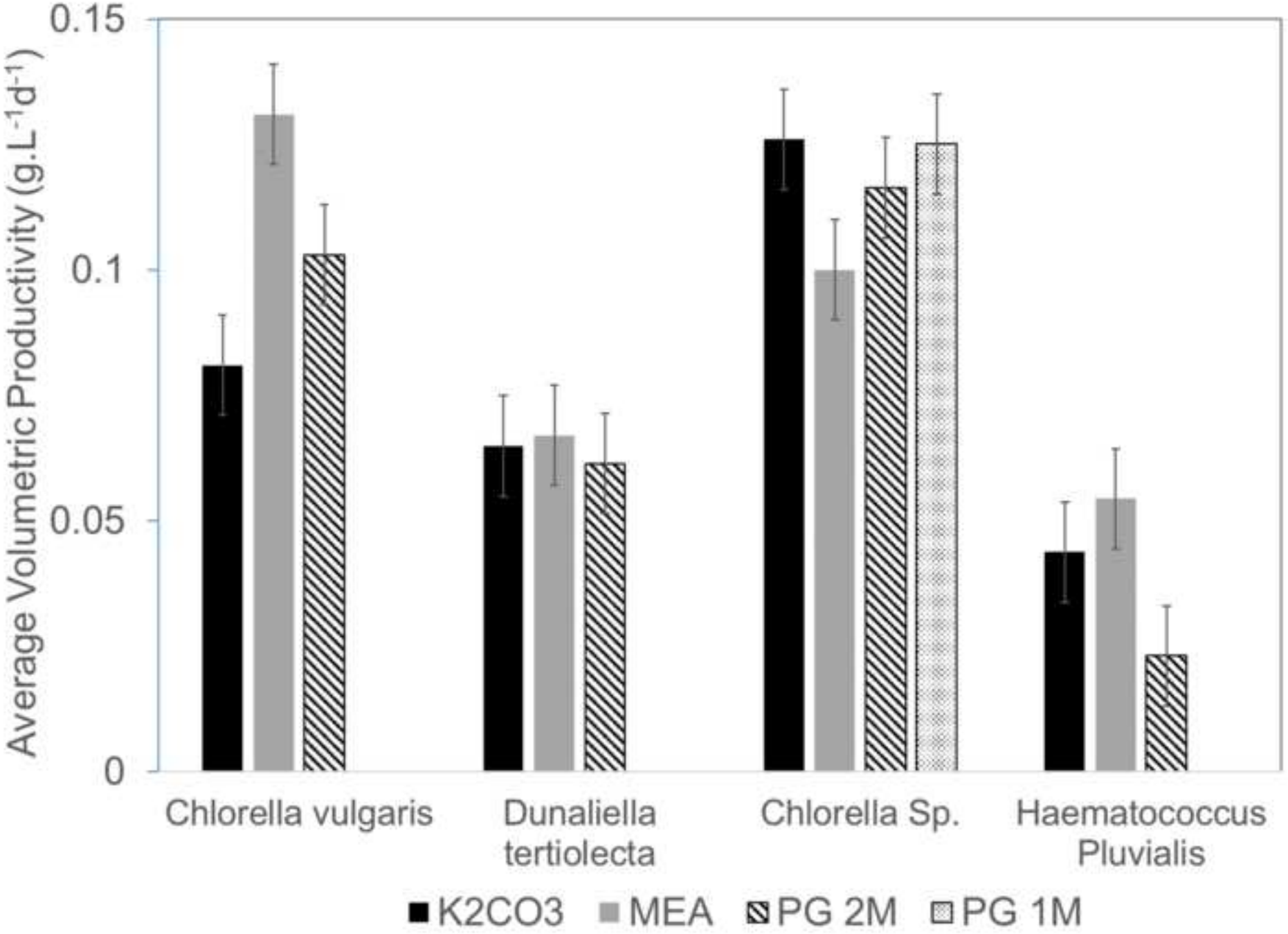

0.15
0.1
0.05
0
Average Volumetric Productivity (g.L-1d-1)
Chlorella vulgaris
Dunaliella tertiolecta
Chlorella Sp.
Haematococcus Pluvialis
K2CO3
MEA
PG 2M
PG 1M

Figure 5

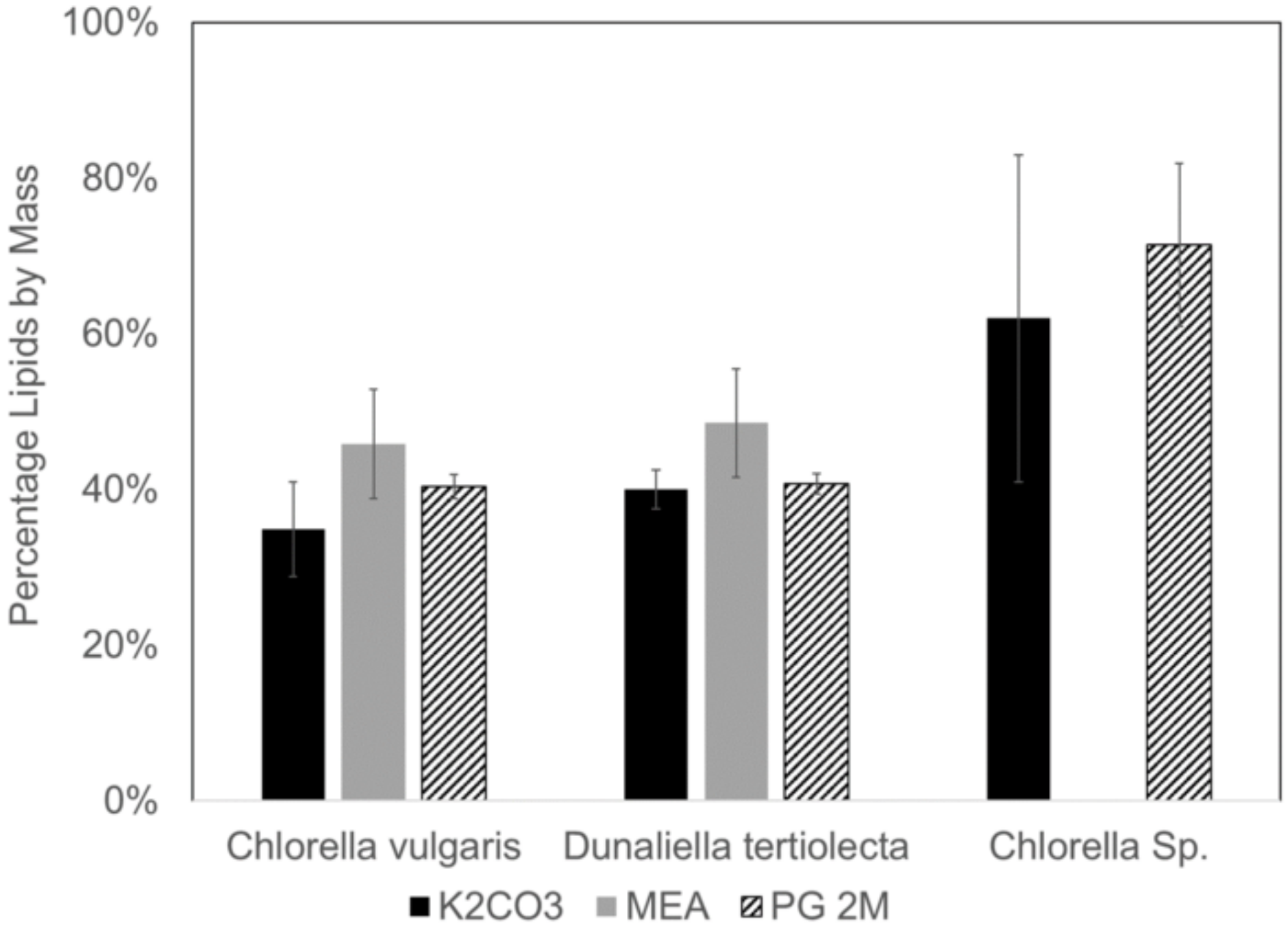
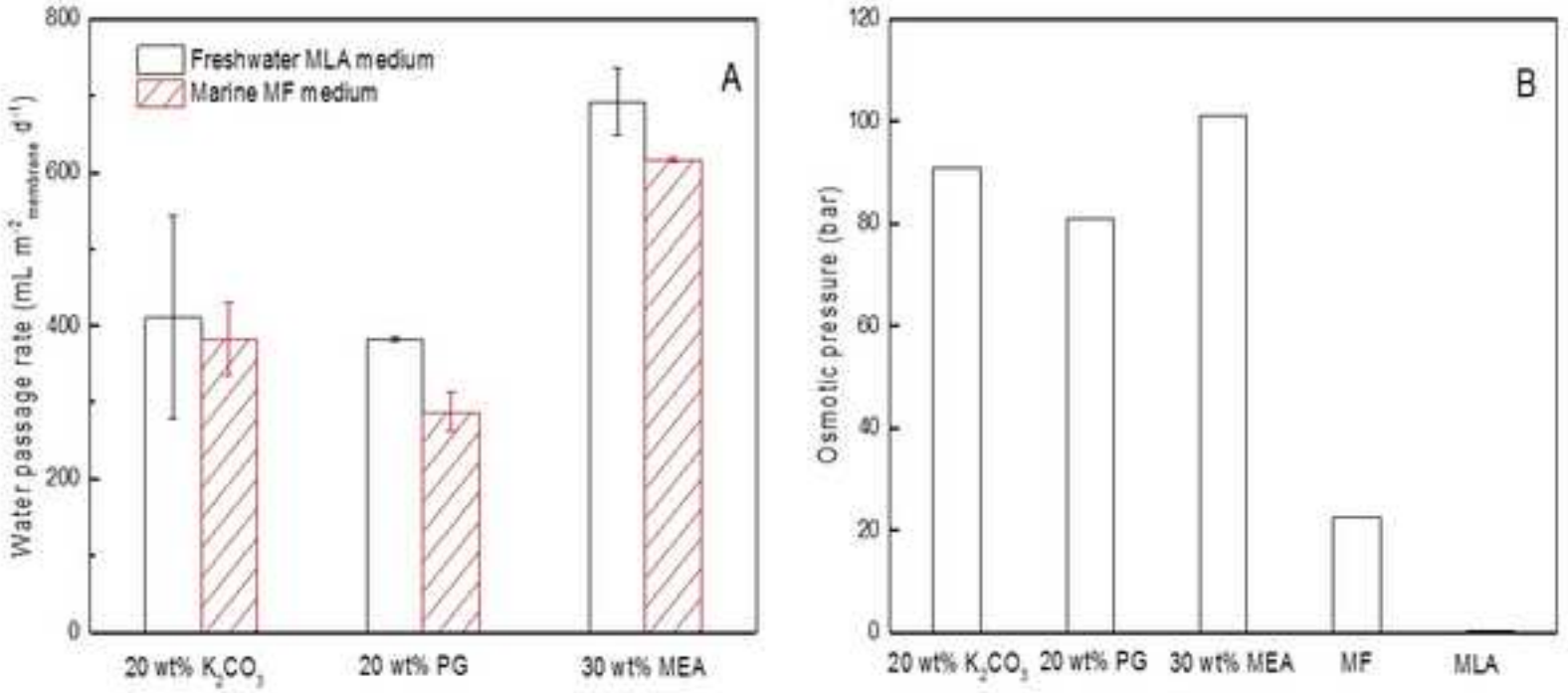

100%
80%
60%
40%
20%
0%
Percentage Lipids by Mass
Chlorella vulgaris
Dunaliella tertiolecta
Chlorella Sp.
K2CO3
MEA
PG 2M

Figure 6


Freshwater MLA medium
Marine MF medium
A
Water passage rate (mL m^{-2} $_{membrane}$ d^{-1})
800
600
400
200
0
20 wt% K_2CO_3
20 wt% PG
30 wt% MEA
B
Osmotic pressure (bar)
120
100
80
60
40
20
0
20 wt% K_2CO_3
20 wt% PG
30 wt% MEA
MF
MLA

Author/s:
Zheng, Q; Martin, GJO; Kentish, SE

Title:
The effects of medium salinity on the delivery of carbon dioxide to microalgae from capture solvents using a polymeric membrane system

Date:
2019-06-01

Citation:
Zheng, Q., Martin, G. J. O. & Kentish, S. E. (2019). The effects of medium salinity on the delivery of carbon dioxide to microalgae from capture solvents using a polymeric membrane system. JOURNAL OF APPLIED PHYCOLOGY, 31 (3), pp.1615-1622. https://doi.org/10.1007/s10811-018-1676-y.

Persistent Link:
http://hdl.handle.net/11343/225554

File Description:
Accepted version