The use of monoethanolamine and potassium glycinate solvents for CO_2 delivery to microalgae through a polymeric membrane system

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Abstract

We have previously shown that a combined system involving solvent absorption, membrane desorption and microalgal cultivation can provide an effective approach to carbon dioxide capture and utilisation (Energy Environ. Sci., 2016, 9, 1074). In this article, we evaluate aqueous solutions of monoethanolamine (MEA) and potassium glycinate for membrane desorption of CO_2, and compare these with our previous work using potassium carbonate. Enhanced growth of *Chlorella* sp. was observed with 20 wt% potassium glycinate at 0.5 CO_2 loading (moles of CO_2 absorbed per mol solvent), while similar growth rates to the control were observed at 0.2 loading. For MEA, algal growth was accelerated at 0.5 loading but was inhibited at 0.2 loading. This was related to the volatile MEA crossing the membrane and poisoning the algae. Considering the kinetics of CO_2 absorption into the solvent, the improvement of microalgal growth and the system stability in case of solvent leakage, amino acids such as potassium glycinate are the ideal solvent for this application.

1. Introduction

Unabated anthropogenic greenhouse gas (GHG) emissions will have catastrophic consequences into the future, including global warming, sea level rise, and more frequent extreme weather events. The CO_2 emissions from stationary power plants during electricity generation represent a large proportion of these GHG emissions. In the U.S.A., for instance, CO_2 emissions accounted for up to 30% of total GHG emissions in 2014 [1]. Several technologies for capturing CO_2 from the flue gas emitted by power plants have been proposed, such as chemical absorption [2, 3], physical adsorption [4], membrane technology [5] and biological mitigation [6-8].

Of these technologies, biological mitigation can both capture CO_2 and produce a range of products such as biofuels, protein feeds, or nutraceuticals such as omega-3 fatty acids and carotenoids [9-11]. Compared to conventional crops, such as sugar cane or soybean, microalgae can be grown at much higher areal productivity, do not require arable land and can be grown to produce a range of high value products [12].

To maximise biomass productivity and solar utilisation, microalgal cultures must not be carbon-limited [13] and therefore need to be supplied with CO_2 from sources such as flue gas or purified CO_2 from power plants. The conventional approach has been to sparge CO_2-rich air directly into the cultures, but this approach has two major practical limitations. Firstly, much of the carbon dioxide escapes from the necessarily shallow algae ponds into the atmosphere. Secondly, the gas compression and transportation from the power plant to potentially vast microalgal ponds requires considerable energy [14]. In order to reduce CO_2 loss, diffusers can be used to form microbubbles that have a longer retention time in the medium [15]. Alternatively CO_2 can be solubilised directly into the medium by pumping gaseous CO_2

through dense membranes [16] to completely avoid CO_2 loss through ventilation. However, these methods cannot avoid the high energy penalty related to the pressure drop resulting from pumping gaseous CO_2.

In our previous work, we proposed a solution to these problems with the use of a CO_2-loaded liquid solvent, which can release the CO_2 through a non-porous polymeric membrane to the microalgal medium. The solvent passes through the inside of these fibres, so that it is not in direct contact with the medium. This approach also provided an energy efficient means of regenerating the capture solvent [17]. The concept of an integrated system of solvent absorption, membrane desorption and microalgal technology was demonstrated by delivering CO_2 from potassium carbonate solutions directly to *Chlorella* sp. cultures using an asymmetric hollow fibre membrane with a polydimethyl siloxane (PDMS) outer layer [17]. We were able to achieve outstanding productivities of up to 0.38 g L^{-1} d^{-1} by avoiding carbon limitation in dense cultures using a 20 wt% potassium carbonate solution with a CO_2 loading of 0.5 or 0.7 (CO_2 loading is defined as the moles of CO_2 absorbed per mole of solvent).

While this approach proved highly effective for microalgal growth, the reaction rate of potassium carbonate with CO_2 is slow [18] and this can mean that the upstream absorption operation becomes difficult. In chemical absorption operations, other solvents, such as MEA (monoethanolamine) and amino acid salts (e.g. potassium glycinate (PG)), have been shown to capture CO_2 with greater reaction rates, making them more practical for this absorption step [19]. MEA is the most widely used chemical solvent for CO_2 capture due to its rapid reaction rate and low cost [20]. Amino acid salts have also been used in commercial capture operations within the Siemens POSTCAP and the BASF Puratreat and Alkazid formulations; and have

attracted research interest due to their fast reaction rate, high cyclic loading capacity, low volatility and degradation stability [3, 21-25].

In this article, we compare these two solvents with potassium carbonate to determine whether they might be as effective for microalgal growth. This would allow the combined system to operate with maximum effectiveness.

2. Materials and methods

2.1. Materials

The solvents used in this study were 30 wt% MEA, 20 wt% PG (2 mol L^{-1}) and 20 wt% potassium carbonate. We chose 30 wt% MEA as this is the concentration most commonly used in the post-combustion carbon capture process [26, 27]. While it would be desirable also to use 30 wt% K_2CO_3, this forms precipitates during CO_2 absorption at atmospheric temperature [28]. Hence, 20 wt% K_2CO_3 was utilized in this study. Amino acid salts within a range from 0.5 mol L^{-1} to 6 mol L^{-1} have been investigated to capture CO_2 [29-32]. We chose 20 wt% PG (2 mol L^{-1}) as being typical of these studies and as it was easily compared with 20 wt% K_2CO_3.

Both MEA and PG contain a primary amine group that reacts with CO_2 to form a carbamate anion and a protonated amine according to Equation (1):

$$2AmH + CO_2 \leftrightarrow AmCOO^- + AmH_2^+ \tag{1}$$

CO_2-loaded MEA was prepared by bubbling pure CO_2 gas into 30 wt% MEA (Chem-supply, 99%) for 30 min to saturate with CO_2. The CO_2 concentration in the solvent was then measured by coulometery (CM5015 Coulometer, UIC). By mixing CO_2-loaded MEA and CO_2-free MEA, 30 wt% MEA with loadings of 0.5 and 0.2 were prepared and checked with coulometery. The loading indicates the extent to which the CO_2 carrying capacity of the solvent is filled. For

MEA solvents this is defined as the moles of all CO_2 carrying species divided by the moles of all MEA carrying species [33]:

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

The initial pH values of 30 wt% MEA with CO_2 loadings of 0.5 and 0.2 were 8.7 and 10.8, respectively.

PG solutions of 20 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) [23]. Pure CO_2 gas was bubbled into this solution for 30 minutes to saturate with CO_2. The total concentration of CO_2 in the solvent was then measured by coulometery (CM5015 Coulometer, UIC). By mixing CO_2-loaded PG and CO_2-free PG, 20 wt% PG solutions with CO_2 loadings of 0.2, 0.5, 0.6 were prepared and then checked with coulometery. The CO_2 loading of 0.6 was included as amino acid salts have been shown to achieve a CO_2 loading of more than 0.5 [34, 35], due to simultaneous bicarbonate formation. The CO_2 loading for PG solvents is defined as [19]:

$$CO_2 \text{ loading in potassium glycinate} =$$

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

The initial pH of 20 wt% PG solvents with CO_2 loadings of 0.2, 0.5, 0.6 were 10.7, 8.8 and 8.3, respectively.

Potassium carbonate solutions of 20 wt% with 0.5 CO_2 loading were prepared by addition of 114.8 g K_2CO_3 (Senator Chemicals, 99.7% purity) and 166.4 g $KHCO_3$ (Univar, 98% purity) to 903.6 g Millipore water [17]. The CO_2 loading for these solutions is defined as:

$$CO_2 \text{ loading in } K_2CO_3 = \frac{[HCO_3^-]}{[K^+]} \qquad (4)$$

The initial pH of 20 wt% potassium carbonate solvent with a CO_2 loading of 0.5 was 9.9.

Composite membranes containing a polysulfone support layer and a thin non-porous polydimethylsiloxane (PDMS) layer coating were used (Airrane, Korea) as previously described [17]

2.2. Strain and cultivation

A marine strain of *Chlorella* sp., isolated from Cooper Creek at Innamincka, South Australia was used in this study [36]. It was cultivated in 500-mL Erlenmeyer flasks with 400 mL of 3% artificial ocean water mix (Ocean Fish, Prodac International, Italy) and Modified-F medium [36] under ambient temperature 25 ±3 ℃ and light intensity of approximately 130 mmol m^{-2} s^{-1} [17]. The initial biomass concentration immediately after inoculation was 0.18 g L^{-1}. Flask openings were covered with vented plastic film to reduce bacterial contamination and water evaporation. The culture flasks were agitated at 120 rpm on an orbital shaker (SS70, Chiltern Scientific, Australia). CO_2-loaded solvents were pumped though the tube side of hollow fibre PDMS membranes immersed in the microalgal medium, as described in our previous study [17]. All experiments were conducted in duplicate flasks.

2.3. Analyses

Samples (10 mL) of the microalgal cultures were taken every two days. Sample pH was monitored by a pH meter (HI 9125, HANNA, Australia, calibrated using pH 4 and 7 buffer solutions). Optical density was determined at 750 nm using a Cary 3E UV-Vis absorbance spectrophotometer (Agilent Technologies, Mulgrave, Victoria, Australia). The total carbon (TC) and dissolved inorganic carbon (DIC) in the culture medium were measured using a Total Organic Carbon Analyser (TOC-VCSH, Shimadzu, Japan) after filtration of the sample through a 0.45-μm syringe filter. Total nitrogen was estimated by UV absorbance at 275 nm and 220 nm using a Cary 3E UV-Vis absorbance spectrophotometer (Agilent Technologies, Mulgrave, VIC, Australia) after filtration of the sample through a 0.45-μm syringe filter [37]. 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)).

The CO_2 concentration of the MEA and PG solvents was monitored by a coulometer (CM5015 Coulometer, UIC). In the coulometer sample flasks, excessive sulphuric acid (10 mL 0.8 mol L^{-1}) is added to acidize the sample, then a CO_2-free carrier gas transported the evolved CO_2 into the reaction cell, where CO_2 was absorbed with monoethanolamine to form a titratable acid. The colour change of the titratable acid was registered by a photodetector which produced a current to generate base electrochemically to neutralize the titratable acid.

Samples (20 mL) of culture were taken at the end of cultivation and filtered through glass microfiber filters (Whatman GF/C 47mm) which were washed once with 20 mL deionized water and dried at 105 ℃ for 16 h [38]. A linear relationship between optical density and dry weight of *Chlorella* sp. was achieved as dry cell weight (g L^{-1}) =0.2727× optical density + 0.1772, R^2 = 0.972.

The CO_2 partial pressures above 20 wt% K_2CO_3 and 20 wt% PG are simulated within Aspen Plus™ with the e-NRTL fluid package as modified by Lee et al. [39].

3. Results

3.1. Effect of different CO_2-loaded solvents on Chlorella sp. growth

Chlorella sp. was cultivated with exposure to only atmospheric CO_2 (control) and in contact with membranes through which MEA, PG or K_2CO_3 solvents at various CO_2-loadings were circulated. The biomass and total nitrogen (TN) concentration (Fig. 1), and the pH, dissolved inorganic carbon (DIC) and total carbon (TC) (Fig. 2) were measured during the experiments. The cultures that were provided CO_2 using any of the solvents at CO_2-loadings of 0.5 had significantly improved biomass growth over the control (Fig. 1A and B). Growth in the culture supplied with MEA at 0.5 loading was comparable with that for K_2CO_3 at 0.5 loading for the first three days, after which it progressively fell behind (Fig. 1A). The cultures with PG at 0.5 loading experienced similar growth rate to cultures with K_2CO_3 at 0.5 loading (Fig. 1B).

The cultures with PG at 0.6 loading also grew faster than the control, but slower than at 0.5 loading (Fig. 1B). However, the use of PG at 0.2 loading did not noticeably enhance microalgal growth, while the cultures grown with MEA at 0.2 loading appeared to be inhibited relative to the control. The maximum specific growth rate μ (d^{-1}) during the initial period of pseudo-exponential growth (i.e. before significant self-shading occurs) and the average and maximum volumetric productivities were determined according to Zheng et al. [17] (Table 1). The maximum specific growth rates and volumetric productivities of the cultures using K_2CO_3 solvent at 0.5 loading were comparable with our previous study [17].
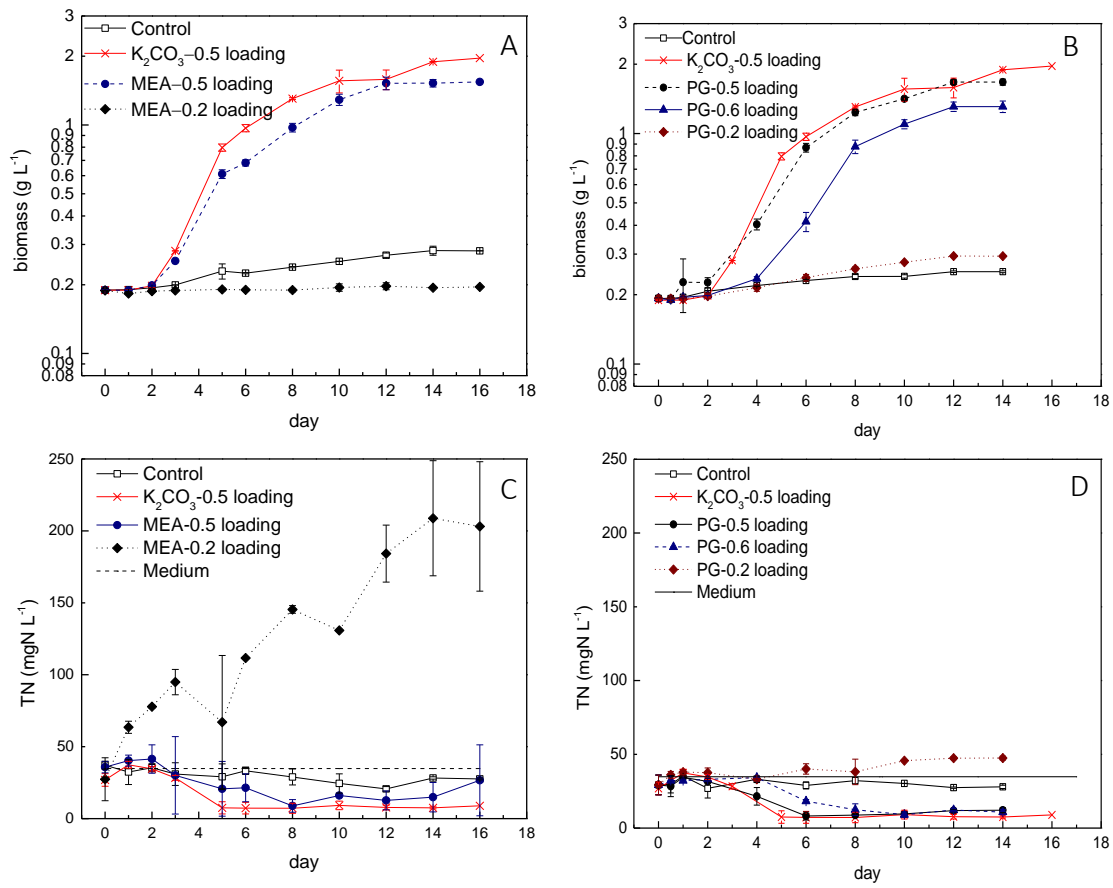
Fig. 1. Biomass concentration (A and B) and total nitrogen (TN) (C and D) in cultures of *Chlorella* sp. with CO_2 supplied by membrane delivery at potassium carbonate of 0.5 loading, MEA of 0.2 loading, 0.5 loading, potassium glycinate (PG) of 0.6, 0.5, 0.2 loading or by atmospheric diffusion only (the control). Error bars represent the standard error of the mean.

Table 1

Comparison of the maximum specific growth rate, μ_{max} and volumetric productivity of

Chlorella sp. cultures grown with different sources of CO_2

	$\mu_{max}{}^{a}$ (d^{-1})	Average volumetric Productivity (g L^{-1} d^{-1})	Maximum volumetric Productivity (g L^{-1} d^{-1})
Control	0.026±0.002	0.0062±0.0005	0.009±0.002
K$_2$CO$_3$-0.5 loading	0.464±0.002	0.126±0.007	0.257±0.008
MEA-0.5 loading	0.37±0.04	0.10±0.01	0.18±0.03
MEA-0.2 loading	n/a	0.002±0.003	0.002±0.001
PG-0.5 loading	0.34±0.001	0.106±0.001	0.23 ± 0.04
PG-0.6 loading	0.33±0.003	0.080±0.003	0.23± 0.01
PG-0.2 loading	0.05±0.01	0.007±0.001	0.011±0.004

[a]The maximum specific growth rates μ (d^{-1}) of cultures with K$_2$CO$_3$ and MEA were calculated with biomass concentrations on day 2 and day 5, and the maximum specific growth rates of cultures with PG of 0.2 and 0.5 CO_2 loadings were based on biomass concentrations on day 2 and day 6, with PG of 0.6 CO_2 loading was based on biomass concentration on day 4 and day 8.

As CO_2 crosses the membrane in the vapor state, it is the CO_2 partial pressure difference between the solvent and the algal medium that determines the driving force for mass transfer. To better understand the capacity of the different solvents to deliver CO_2 to the algal cultures at different loadings, the CO_2 partial pressures above 30 wt% MEA, 20 wt% K$_2$CO$_3$ and 20 wt% PG were determined as a function of loading at 25 °C (Fig. 3). The CO_2 partial pressures

in all three solvents at CO_2-loadings of 0.5 are similar in magnitude (around 10^3 Pa). For these solvents, the pH of the microalgal medium fell significantly during the initial lag period (Fig. 2A and 2B), as more CO_2 was delivered to the medium than could be consumed. Once biomass growth accelerated, the pH of the microalgal medium increased to between 7 and 8; a suitable range for microalgal growth [40]. For all three solvents at these loadings, the DIC increases continuously, indicating that the supply of CO_2 continued to exceed the culture demands (Fig. 2C, D).

With a CO_2 partial pressure of around 10^4 Pa in the PG solvent with 0.6 loading (Fig. 3), the rapid transfer of CO_2 to the medium sharply decreased the pH from 8.4 to 5.6 in the first half day (Fig. 2B). As the cultures grew, the demand for CO_2 increased so that the pH increased from 5.6 to 6.1 at day 2, and to 7.0 at day 4. However, the low pH during the first two days resulted in a prolonged lag phase compared with that which occurred with the PG solvent at 0.5 loading. After the lag phase, the cultures with PG at 0.5 and 0.6 loading grew at a similar specific growth rate (0.33 d^{-1}, 0.34 d^{-1}) for four days. This suggests that without a means of providing external pH control, there is likely an upper limit in the CO_2 loading of PG that can be applied to avoid a lag in culture growth due to oversupply of CO_2.

At 0.2 loading, the PG solvent initially provides a very low CO_2 partial pressure of around 6 Pa (Fig. 3), which is below the CO_2 partial pressure of sea water at pH 8.3 (around 39 Pa [41]). Hence in the first day, CO_2 transfer could, in fact, be in the opposite direction, from the growth media and to the solvent. Correspondingly, in the first two days with PG solvent at 0.2 loading, the DIC concentration in the cultures decreased slightly, as the CO_2 transfer rate could not meet the rate required for microalgal growth. Concomitantly, the pH rapidly increased to 9, which is above the optimum value for microalgal growth. In the following days, as CO_2 was

continuously transferred to the medium, the low CO_2 transfer rate limited growth and the DIC remained around 10 mg L^{-1}, a similar level to the control. In this case, the CO_2 that was made available to the algae may have come from the atmosphere above the cultures, as with the control, rather than through the membrane.

The cultures with MEA at 0.2 loading exhibited no growth. As with PG, MEA also provides a very low CO_2 partial pressure (around 2 Pa) (Figure 3) to drive mass transfer. If this had resulted in an absence of CO_2 in the growth media, it might explain a reduced rate of growth in the cultures using this solvent. However, the cultures exhibited no growth whatsoever, and measurements of DIC concentration (Fig. 2C) indicate that CO_2 was available but that it was not consumed by the algae.
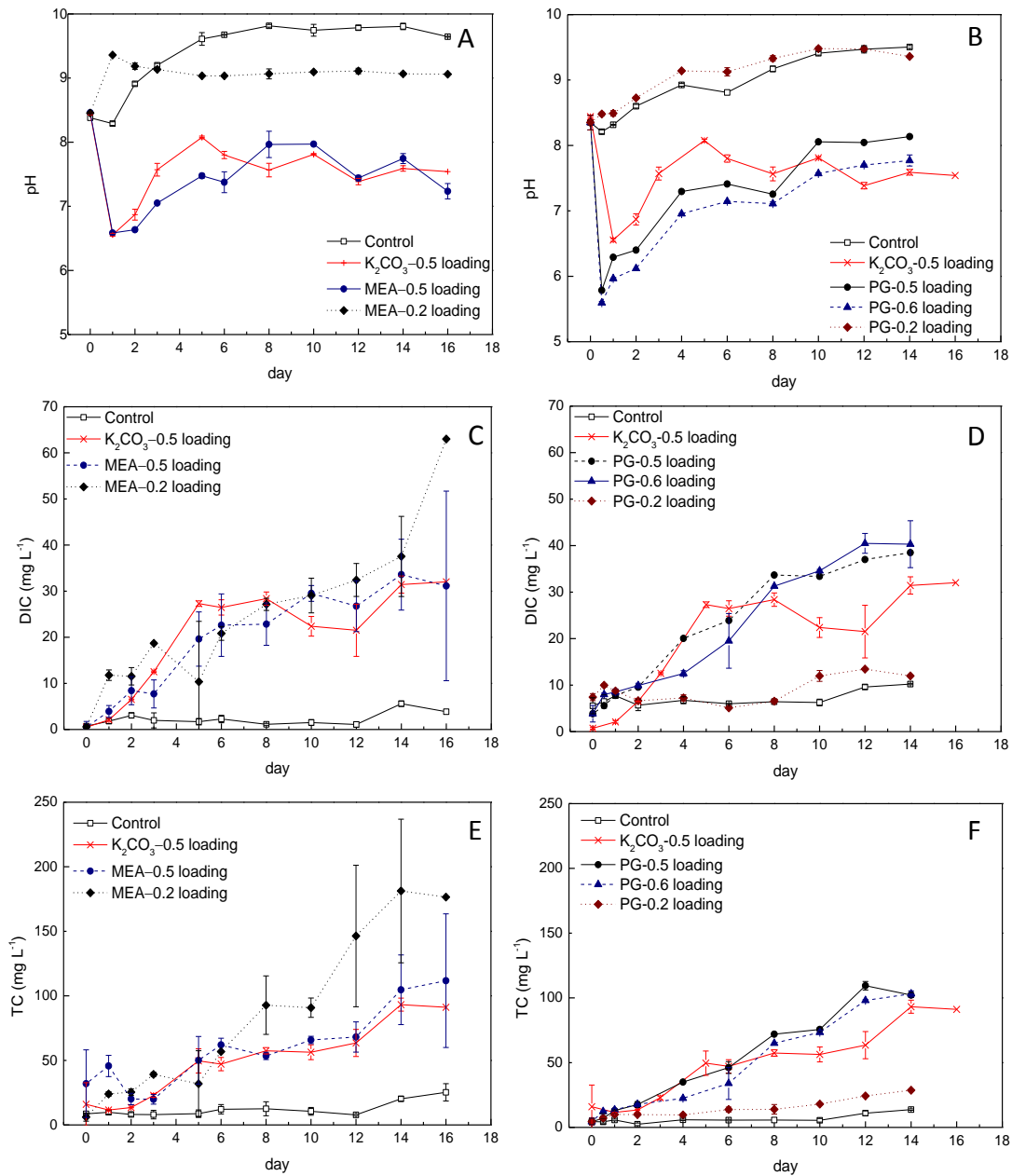
Fig. 2. pH (A and B), dissolved inorganic carbon (C and D) and total carbon (E and F) in the microalgae medium with CO_2 supplied by different CO_2 loaded solvents or by atmospheric diffusion only (the control). Error bars represent the standard error of the mean.
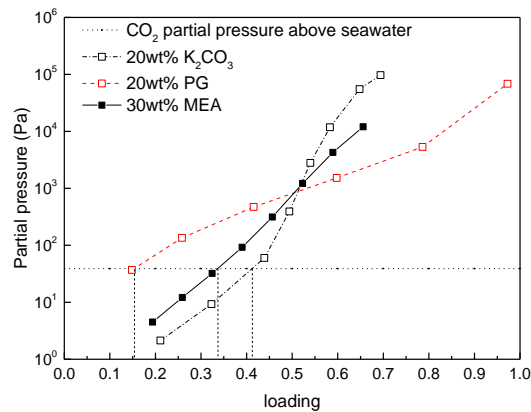
Fig. 3. CO_2 partial pressure of 30 wt% MEA, 20 wt% K_2CO_3 and 20 wt% PG as a function of the CO_2 loading, compared to seawater at 25 ℃ and pH 8.3. The seawater [41] and the MEA [42] data are from the published literature. The K_2CO_3 and PG data are simulated within Aspen Plus™ with the e-NRTL fluid package as modified by Lee et al. [39]

3.2. Solvent permeation

The complete lack of growth exhibited by the cultures using MEA at 0.2 loading could not be explained by unavailability of a carbon source. Another possibility is that MEA was able to pass across the membrane and inhibit the algae. Consistent with an accumulation of MEA in the growth media, the total nitrogen (TN) and total carbon (TC) both increased markedly when this solvent was used (Figs. 1C and 2E, respectively). In contrast, the TN in the K_2CO_3 and PG solvents at 0.5 loading and the control culture decreased to effectively zero over the growth period (Fig. 1C and 1D), due to uptake by the algae, in accordance with the previous study [17].

MEA is a volatile solvent, with unloaded 30 wt% MEA having a vapour pressure of 2800 Pa at 25 ℃ [42]. The MEA solvent at 0.2 loading has 60% free, uncharged MEA, which is volatile, and can pass though the PDMS membrane, causing the TN and TC concentrations in the

microalgal medium to increase. In contrast, in a solvent at 0.5 loading, the MEA should be completely in the charged forms ($HOCH_2CH_2NH_3^+$ and $HOCH_2CH_2NHCOO^-$, as per Eq. (1)) and so should not permeate. Only through the reversal of Eq. (1) can a small amount of uncharged MEA be released in the MEA-CO_2-H_2O system.

To determine the rate of MEA leakage through the PDMS membrane, MEA solvents of different CO_2 loading were pumped through the tube side of membranes submerged in purified water (Millipore Elix). The TN concentration in the RO water increased with time, with higher rates observed at decreased solvent loadings (Fig. 4A). With loadings of 0.2 and 0.5, the average rates were 4.3 mgN L^{-1} d^{-1} and 0.9 mgN L^{-1} d^{-1}, respectively. The leakages from potassium glycinate solvents were also determined (Fig. 4B). With these solvents at 0.2 and 0.5 loading, the average rates were 0.9 mgN L^{-1} d^{-1} and 0.2 mgN L^{-1} d^{-1}, respectively, which are much lower. The higher rate of leakage with the 0.2 loaded potassium glycinate solvent is consistent with a slight increase in TN observed during microalgae growth (Fig. 1D), and can be explained by small concentrations of free glycine at the solution pH of 10.8 [23].
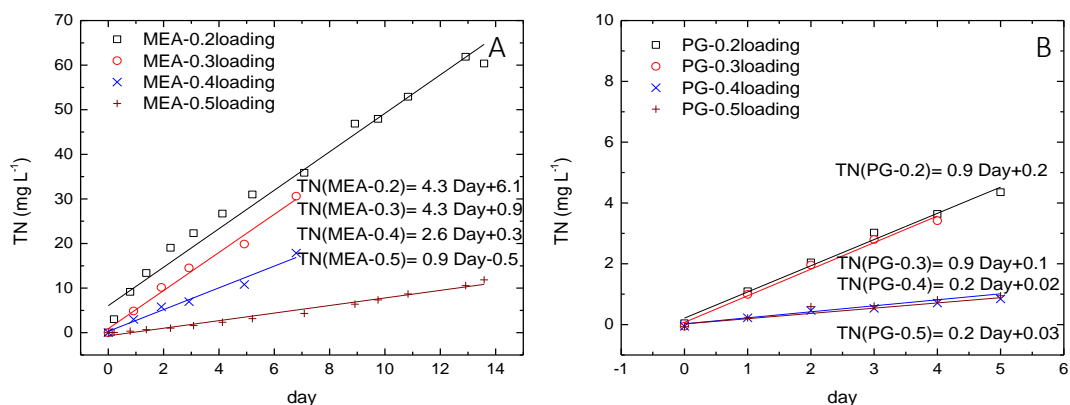
Fig. 4. Total nitrogen in RO water when MEA (A) and potassium glycinate (B) solvents of variable loading are passed though the tube side of the immersed PDMS membranes.

3.3. Effect of MEA and PG toxicity on the growth of Chlorella sp.

The results presented above indicate that free MEA, present at low loadings, can leak through PDMS membranes and accumulate in the algal growth medium. Some studies have shown that low concentrations (up to 300 ppm) of MEA can be used as a CO_2 absorbent in the medium to enhance CO_2 solubility and improve the growth of various microalgae (*Scenedesmus* sp., *Spirulina* sp.) [43, 44]. However, MEA is a toxic chemical. If present at high enough concentration, this may cause the lack of growth observed in the cultures grown with MEA at 0.2 loading. To confirm this possibility, MEA was added directly to microalgae cultures (with no added CO_2 and an initial biomass concentration of 0.18 g L^{-1}) on a daily basis at rates corresponding to the rates of MEA permeation through the membrane system determined above (Fig. 4A) (0.9 mgN L^{-1} d^{-1}, 2.6 mgN L^{-1} d^{-1} and 4.3 mgN L^{-1} d^{-1}). Growth of *Chlorella* sp. was inhibited compared to the control, even at the lowest rate of MEA addition, and at the higher rates algal death occurred (Fig. 5A), demonstrating the toxicity of MEA to *Chlorella* sp. In the previous results, growth of *Chlorella* sp. was enhanced when MEA of 0.5 loading was

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used (Fig. 1A), despite the transfer of toxic MEA into the growth medium. However, in this case the culture was not CO_2-limited and therefore able to grow rapidly, presumably utilising some of the MEA as a nitrogen source, enabling the concentration of MEA in the medium to be kept below toxic levels. The relatively constant TN in the culture grown in MEA at 0.5 loading (Fig. 1C) is consistent with this, as is the rising level of TN in the culture of 0.2 loading (Fig. 1C) which was inhibited (Fig.1A).

To determine if glycine is also toxic to *Chlorella* sp., glycine and CO_2-loaded potassium glycinate were added directly to microalgal cultures (with no added CO_2 and an initial biomass concentration of 0.28 g L^{-1}) on a daily basis at rates corresponding to the rates of glycine permeation through the membrane system determined above (Fig. 4B), 0.2 mgN L^{-1} d^{-1} and 0.9 mgN L^{-1} d^{-1}. To compare with MEA, the highest rate of 4.3 mgN L^{-1} d^{-1} was also chosen. Rather than being inhibited, the growth of *Chlorella* sp. improved with added glycine and CO_2 loaded potassium glycinate. This suggests that, rather than being toxic to the algae, these two solvents can be utilised as carbon and nitrogen sources for microalgal growth [45].
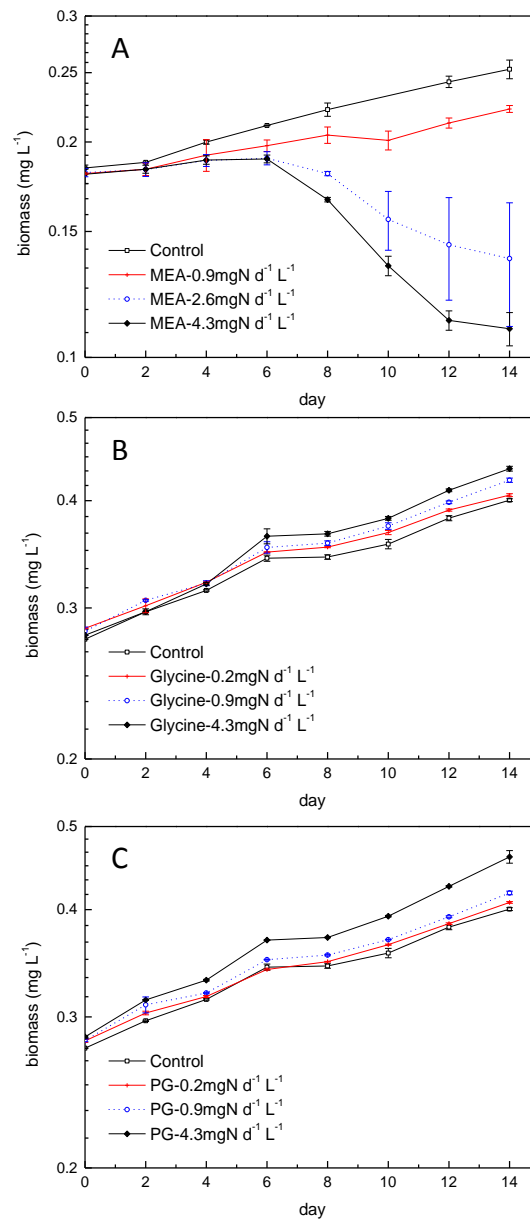
Fig. 5. Growth curve of *Chlorella* sp. when pure MEA (A), pure glycine (B), or CO_2-loaded potassium glycine (C) are added directly to the medium. Error bars represent the standard error of the mean.

4. Discussion

The results above have shown that the solvents MEA, PG and potassium carbonate can all enhance microalgal growth when provided at 0.5 CO_2 loading. However, for practical implementation, other issues need to be considered.

As a solvent for capturing CO_2, potassium carbonate has several advantages. It has less human toxicity and eco-toxicity compared with MEA [46]. It is not readily degraded by oxygen or impurities (NO_X, SO_X) in the flue gas that is used as a source of CO_2 and requires less energy for solvent regeneration [46]. Further, as a charged compound, potassium carbonate does not permeate through the membrane, which means it cannot contaminate the medium. However, potassium carbonate reacts slowly with CO_2, which inhibits its practical implementation [3].

MEA is more widely used in CO_2 capture, due to its faster reaction rate. However, MEA is corrosive and can be degraded through irreversible reactions with oxygen, NO_X and SO_X in the flue gas [47]. As solvent loss occurs via evaporation and via these degradation reactions, a makeup stream of around 1.6 kg $MEA/tCO_{2captured}$ is typically needed [48]. Formaldehyde and nitrosamines, which are products of MEA degradation, are carcinogenic [46]. Further, we have shown in this work that the lean solvent (0.2 loading) inhibited microalgal growth due to permeation of MEA through the membrane, which was toxic to the microalgae. In a full scale system, membrane failure may sometimes occur, causing localised high levels of this solvent, which would also cause the culture to die.

Potassium glycinate has a similar reaction rate towards CO_2 as MEA, but has lower oxidative degradation, is less volatile and has less environment impact [3]. As a carbon source, PG solvents at 0.5 loading can result in strong microalgal growth when used in the present

arrangement. Implementation will require consideration of the optimal range of loadings with which to operate to avoid a low-pH-induced lag at too high a loading (e.g. 0.6 loading here), or suboptimal growth at too low a loading (e.g. 0.2 loading here). The valid range of loadings could presumably be increased by operating in a counter-current mode in which the supply were better matched to the demand (e.g. the inlet solvent with the highest CO_2 loading would be used in the ponds with the highest concentration of algae and vice versa). Further, the low rate of permeation of PG into the medium at low loadings did not have a harmful effect on the microalgae. In fact, the permeated solvent slightly improved microalgae growth by serving as a carbon and nitrogen source.

5. Conclusion

CO_2 can be effectively delivered to microalgae ponds through a membrane system. Three solvents (MEA, potassium glycinate and potassium carbonate) of 0.5 CO_2 loading have been demonstrated to enhance *Chlorella* sp. growth. Among these three solvents, potassium glycinate, or a comparable amino acid, would be the most suitable solvent for this process, due to its low volatility, low toxicity and their rapid reaction rate with CO_2.

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