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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 (PG) for membrane desorption of CO_2, and compare these with our previous work using potassium carbonate (K_2CO_3). Enhanced growth of *Chlorella* sp. was observed with 20 wt% PG at 0.5 CO_2 loading (moles of CO_2 absorbed per mol solvent) relative to a baseline control in which carbon dioxide was only available from atmospheric diffusion. Similar growth rates to the control were observed for PG 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 PG 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 (K_2CO_3)

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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% K_2CO_3 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 K_2CO_3 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 monoethanolamine (MEA) 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 K_2CO_3 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% K_2CO_3. 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 utilised 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 Eq. (1):

$$2AmH + CO_2 \leftrightarrow AmCOO^- + AmH_2^+ \quad (1)$$

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 (x) 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]:

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

30 wt% MEA of 0.2 and 0.5 CO_2 loading is equal to 1 mol and 2.5 mol $_{CO2absorbed}$ L^{-1}, respectively. The initial pH values of 30 wt% MEA with CO_2 loadings of $x = 0.2$ and $x = 0.5$ were 10.8 and 8.7, 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 min 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 $x = 0.2$, 0.5, 0.6 were prepared and then checked with coulometery. The CO_2 loading of 0.6 was included since 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]:

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

20 wt% PG of $x = 0.2$, 0.5, 0.6 CO_2 loading is equal to 0.4, 1.0 and 1.2 mol $_{CO2absorbed}$ L^{-1}, respectively. The initial pH of 20 wt% PG solvents with CO_2 loadings of $x = 0.2$, 0.5, 0.6 were 10.7, 8.8 and 8.3, respectively.

K_2CO_3 solutions of 20 wt% with $x = 0.5$ 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:

$$x = \frac{[HCO_3^-]}{[K^+]} \quad (4)$$

20 wt% K_2CO_3 of $x = 0.5$ CO_2 loading is equal to 0.85 mol $_{CO2absorbed}$ L^{-1}. The initial pH of 20 wt% K_2CO_3 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 (MF) medium [36], containing 33 mg-N L^{-1} as nitrate and 3.6 mg L^{-1} of total phophorus. The cultures were cultivated under ambient temperature 25 ± 3 °C and continuously exposed to light at an incident intensity of approximately 130 μmol 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