Algal remediation of CO$_2$ and nutrient discharges: a review. Revised submission

Algal remediation of CO$_2$ and nutrient discharges: a review

Simon Judd[1,3*], Leo J.P. van den Broeke[1], Mohamed Shurair[1], Yussuf Kuti[1], and Hussein Znad[2]
[1]Department of Chemical Engineering, Qatar University; [2]Department of Chemical Engineering, Curtin University; [3]Cranfield Water Science Institute, Cranfield University
*corresponding author, simon.judd@qu.edu.qa

Abstract

The recent literature pertaining to the application of algal photobioreactors (PBRs) to both carbon dioxide mitigation and nutrient abatement is reviewed and the reported data analysed. The review appraises the influence of key system parameters on performance with reference to (a) the absorption and biological fixation of CO$_2$ from gaseous effluent streams, and (b) the removal of nutrients from wastewaters. Key parameters appraised individually with reference to CO$_2$ removal comprise algal speciation, light intensity, mass transfer, gas and hydraulic residence time, pollutant (CO$_2$ and nutrient) loading, biochemical and chemical stoichiometry (including pH), and temperature. Nutrient removal has been assessed with reference to hydraulic residence time and reactor configuration, along with C:nutrient ratios and other factors affecting carbon fixation, and outcomes compared with those reported for classical biological nutrient removal (BNR).

Outcomes of the review indicate there has been a disproportionate increase in algal PBR research outputs over the past 5-8 years, with a significant number of studies based on small, bench-scale systems. The quantitative impacts of light intensity and loading on CO$_2$ uptake are highly dependent on the algal species, and also affected by solution chemical conditions such as temperature and pH. Calculations based on available data for biomass growth rates indicate that a reactor CO$_2$ residence time of around 4 hours is required for significant CO$_2$ removal. Nutrient removal data indicate residence times of 2-5 days are required for significant nutrient removal, compared with <12 hours for a BNR plant. Moreover, the shallow depth of the simplest PBR configuration (the high rate algal pond, HRAP) means that its footprint is at least two orders of magnitude greater than a classical BNR plant. It is concluded that the combined carbon capture/nutrient removal process relies on optimisation of a number of process parameters acting synergistically, principally microalgal strain, C:N:P load and balance, CO$_2$ and liquid residence time, light intensity and quality, temperature, and reactor configuration. This imposes a significant challenge to the overall process control which has yet to be fully addressed.

Keywords   Algae, photobioreactor, CO$_2$, nutrients, wastewaters

1   Introduction

1.1   *Algae for carbon dioxide mitigation*

Mitigation of carbon dioxide through its capture, utilisation and storage has undergone rapid development over the past 20 years, with research and development originally precipitated by the realisation of the impact of CO_2 as the single largest contributor to global warming (Hoyt, 1979). Various measures exist for CO_2 mitigation generally and utilisation specifically (Fig. 1), including enhanced oil and gas recovery (EOR and EGR, the latter including coal-bed methane - ECBM), CO_2 conversion to chemical feedstock and fuels, biological conversion (photosynthesis), and CO_2 mineralisation for the production of materials (Laumb et al, 2013; Hasan et al, 2014). These methods are primarily focussed on CO_2 utilisation following capture; only biological conversion is capable of direct CO_2 mitigation. Utilisation of CO_2 as a feedstock for other production processes, however, offers opportunities to offset part of the significant capital investment associated with capturing the CO_2.
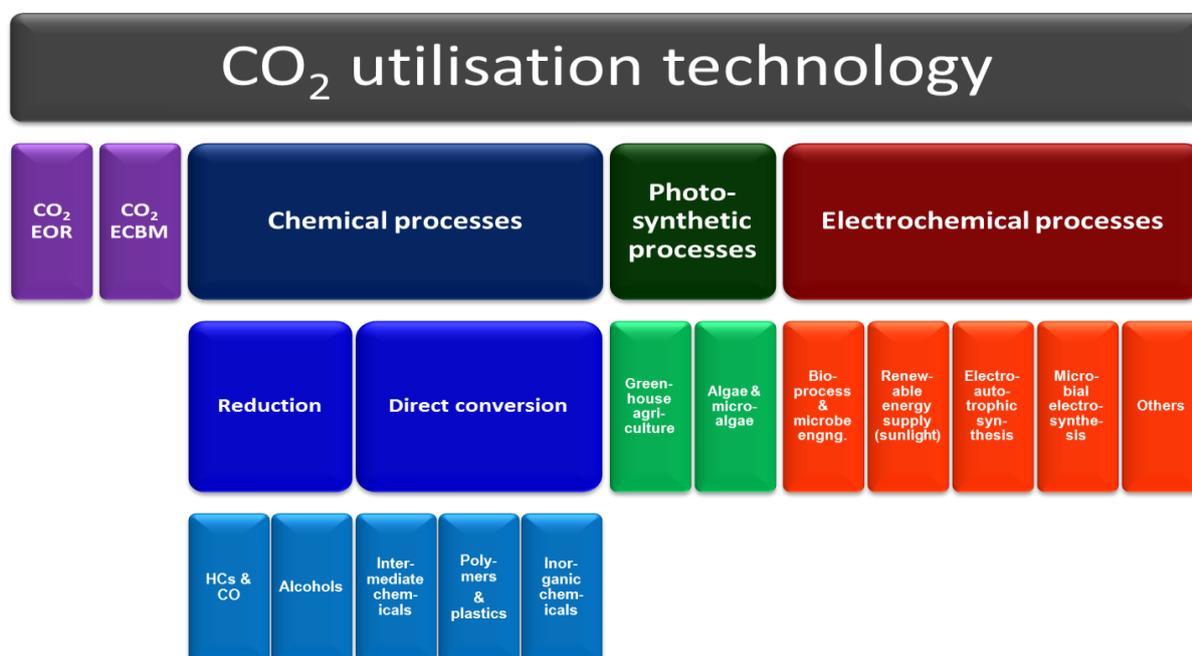
Figure 1: CO_2 utilisation, adapted from Laumb et al (2013)

The use of algae for CO_2 capture and utilisation offers a number of benefits over alternative methods for CO_2 mitigation. Firstly, the method is inherently efficient and sustainable, analogous to conventional biological wastewater treatment, since the biological process requires only the food source (the carbon) and ambient temperatures and daylight to be sustained. The main product, the algal biomass, has a market value and can also be reused for biofuel, including biodiesel, biomethane and biohydrogen (Brennan and Owende, 2010; Scott et al, 2010; Cho et al, 2011), animal feed (Chauton et al, 2015) or other high-value products (Borowitzka, 2013; Lopes da Silva et al, 2014). The latter include proteins and various types of pigment (chlorophyll, carotenoids), and products of a significant global market size such as fatty acids. Indeed, it has been noted (Lundquist et al, 2010; Batten et al, 2013) that the economic case for PBR technology relies largely on the cost benefit offered by the generation of these high-value products: PBRs appear to be uneconomical, even under the most favoured conditions, solely for pollutant removal from aqueous and gaseous waste streams (Acien Fernandez et al, 2012ab).

PBR technology has other attractive features. The reactor is relatively uncomplicated - at its most basic level simply a pond system - is robust to changes in CO_2 load and is fully scale-able. The process technology design is flexible, can use almost any source of CO_2 and can be integrated and/or combined with other processes - including wastewater treatment for organic carbon and nutrient removal. Against this, the relatively slow rate of CO_2 assimilation (compared with conventional biological treatment processes for organic carbon and nutrient removal from municipal wastewaters) means that comparatively large land areas are required.

1.2   Algae for nutrient removal

The growing of algae from a municipal wastewater feed for treatment purposes was investigated as early as the 1950s (Oswald et al, 1953), with the concept of using wastewater as a medium for algae-based biofuel production reported in the seminal close-out report for the Aquatic Species Program (ASP) conducted from 1978 to 1996 (Sheehan et al, 1998). The use of algae for mitigation of the nutrients phosphate, nitrate and ammonia in wastewater treatment has been also the subject of study since around the mid-1970's (Bosch et al, 1974; Yun et al, 1977) as a means of combatting eutrophication (Gavrilescu and Chisti, 2005; Liang et al, 2013). Whilst there are established biological methods for nitrogen and phosphorus (N and P) removal from wastewater, so-called biological nutrient removal (BNR), this classically demands supplementary sludge transfer between aerobic, anoxic and anaerobic regions (Van Loosdrecht et al, 1997; Mulkerrins et al, 2004). More recently, however, BNR has been demonstrated in a single process step through the development of very specific biochemical conditions through extensive acclimation and rigorous process control (Daigger and Littlejohn, 2014). There is nonetheless often an additional requirement for chemical dosing with iron or aluminium-based coagulants to obtain the required P removal (De Gregorio et al, 2010; Li and Brett, 2012). The use of PBRs for the duty of nutrient removal provides an economical and environmentally sustainable alternative, combined as it is with bioenergy and bio-products production and CO_2 mitigation (Sheehan et al, 1998; Clarens et al, 2010; Zhou et al. 2011, 2012a).

1.3   Research trends in algae

An indication of the relative scientific importance of the two different aspects of algal PBRs can be surmised through the use of search engines for examining scientific publications databases, such as *SCOPUS* and *Web of Knowledge*. Searches of keywords appearing in such databases for search terms based on algae (including micro-algae), water (including wastewater) and carbon dioxide (including CO_2 and "flue gas") can be used to identify the number of relevant papers.

A consideration of all research papers dating back to the mid-1960s reveals research articles encompassing water and algae (water ∩ algae) to be about twice as numerous and those based on water ∩ carbon dioxide and ten times more in number than algae ∩ carbon dioxide (Fig. 2a). The application of algae bioreactors for carbon capture appears to be a relatively recent area of study, with a concerted research effort only evident from 1990 onwards (Fig. 2b). Whilst the number of research articles whose keywords encompass all three topics are small compared to those for the individual sets, the publication rate appears to be rapidly increasing. The number of research articles relating to algae, water and CO_2 as discrete topics have all increased at a compound annual growth rate of 6.4-6.7% per year on average since the mid-1960s, with those based on water unsurprisingly far outnumbering those focused on the other two subject areas (Fig. 2a). Those encompassing either all three topics (algae ∩ carbon dioxide ∩ water) or just algae ∩ carbon dioxide, whilst much smaller in number have both increased at a growth rate of

25-30% per year since around 2007 (Fig. 2b) – a growth rate four times higher than that of the individual sets.

(a)	(b)
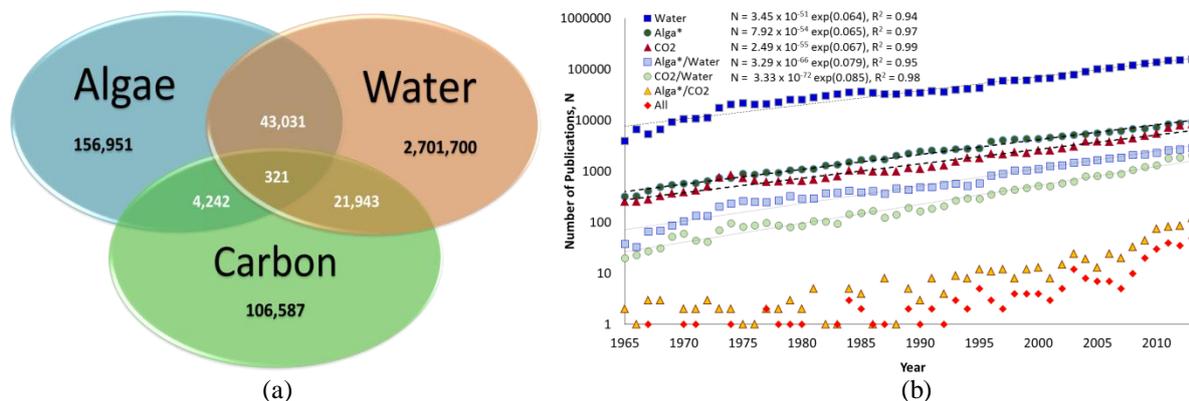
Figure 2: Summary of research articles in key subject areas: (a) total, and (b) by year, according to SCOPUS, based on the search terms of *alga* (including *micro-alga* and *microalga*), *water* (including *wastewater* and *effluent*) and *carbon dioxide* (including CO$_2$ and "*flue gas*")

An indication of the primary topics of interest within the 321-fold papers based on all three topics can be provided by a *Wordle* diagram (www.wordle.com) constructed from the keywords of the articles (Fig. 3). The key search terms (Fig. 2) were excluded from the Wordle analysis, and the words manually normalised (Santos et al, 2012) as follows:
- removal of all upper-case letters;
- conversion of plurals to singular;
- aggregation of all types of PBR configuration into a single term "photobioreactor";
- aggregation of all types of strains of an algal species, e.g. *Chlorella vulgaris* or *Chlorella sp*, into a single term, e.g. "chlorella";
- delineation of the terms "bioenergy", "biogas", "biodiesel" and "biofuel".

Figure 3: Research topics associated with algae ∩ carbon dioxide ∩ water articles (from SCOPUS)

According to Figure 3 published work has been based primarily on the *Chlorella* genus and on PBRs, as observed in recent reviews of algal biomass production and CO$_2$ fixation (Ho et al, 2011; Zhao and Su, 2014; Zeng et al, 2015). There has also been a preponderance of biofuel-related papers in this area (Brennan and Owende, 2010; Scott et al, 2010; Lopes da Silva et al, 2014), underlining one of the key attractions of algal-based mitigation technologies. *Chlorella* is favoured due to its high growth rate (or productivity) - up to 1.2 g/(L.d) under optimum conditions (Cheng et al, 2006; Chiu et al, 2008) - and ability to assimilate CO$_2$ at relatively high

concentrations - up to 100%, according to Concas et al, 2012. However, biological fixation of CO_2 is highly dependent on operating conditions such as CO_2 loading, pH, temperature, light intensity, and medium composition, with first two of these being inter-related (Section 2.4).

Various algal reactor technologies have been investigated, with designs based on either open or closed systems (Table 1) and with various configurations of the latter (Fig. 3). The general trend is for increasing intensivity with increasing complexity of design and/or flow channels. Designs have included revolving systems (Gross and Wen, 2014), air-lift (Cattaneo et al., 2003; Pirouzi et al, 2014) and membrane-sparged systems (Fan et al, 2008), all ostensibly designed to improve CO_2 mass transfer (Section 2.3) and thus productivity.

Table 1:   PBR system facets, adapted from Sudhakar et al, 2011 and Bermudez et al, 2014.

Parameter	Open	Closed
Design complexity	Lower	Higher
Control	Poor	Good
Cost	Lower	Higher
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 utilisation	Poor	Very high
CO_2 losses to atmosphere	High (up to 38%*)	Almost none
Typical growth rate ($g/m^2/day$)	Low: 10-25	Variable:1-500
Area requirement	Large	Smaller
Depth/diameter of water	0.3m	0.1m
Surface: volume ratio	~6	60-400
Cleaning	None	Required
Bimass quality	Variable	Reproducible
Harvesting efficiency	Low	High
Harvesting cost	Higher	Lower
Most costly operating function	Mixing	Oxygen and temperature control
Hydrodynamic stress on algae	Very low	Low-moderate
Gas transfer control	Low	High

*Douchal et al, 2005.

The PBR process may then be operated in either batch or continuous mode, with the algal biomass being recovered as a useful product. As with conventional sewage treatment, biomass-water separation then takes place either by simple sedimentation, the predominantly preferred method (Milledge and Heaven, 2013; Sirin et al, 2013), or occasionally by membrane separation (Gao et al, 2015; Drexler and Yeh, 2014; Marbelia et al, 2014). For steady-state systems the hydraulic and solids (or biomass) retention times, and thus the algal biomass concentration in the reactor, can be controlled prior to harvesting of the algae, which accounts for 20-30% of the total costs (Barros et al, 2015). However, the research has predominantly been based on batch systems.

It is of interest to assess the state of the art of algal PBR technology as it relates to both carbon capture and water treatment, and specifically nutrient removal. Thus far the precise facets required of the technology for accomplishing these two key aims have not been summarised in a single review, and yet evidence suggests (Fig. 2b) that these two applications have been of increasing significance in recent years, with interest possibly originally precipitated by landmark international legislation, such as the 1992 United Nations Framework Convention on

Climate Change (UNFCCC) and the subsequent 1997 Kyoto Protocol. Publications of interest can be roughly divided into those based solely on carbon and those aiming to purify a wastewater stream. Although there are additionally a significant number of papers focused on the production of biofuel and other high-value products, particularly since the turn of the decade (Brennan and Owende, 2010; Scott et al, 2010; Borowitzka, 2013; Markou and Nerantzis, 2013; Lopes da Silva et al., 2014; Chauton et al, 2015), this area was considered outside the scope of this review.
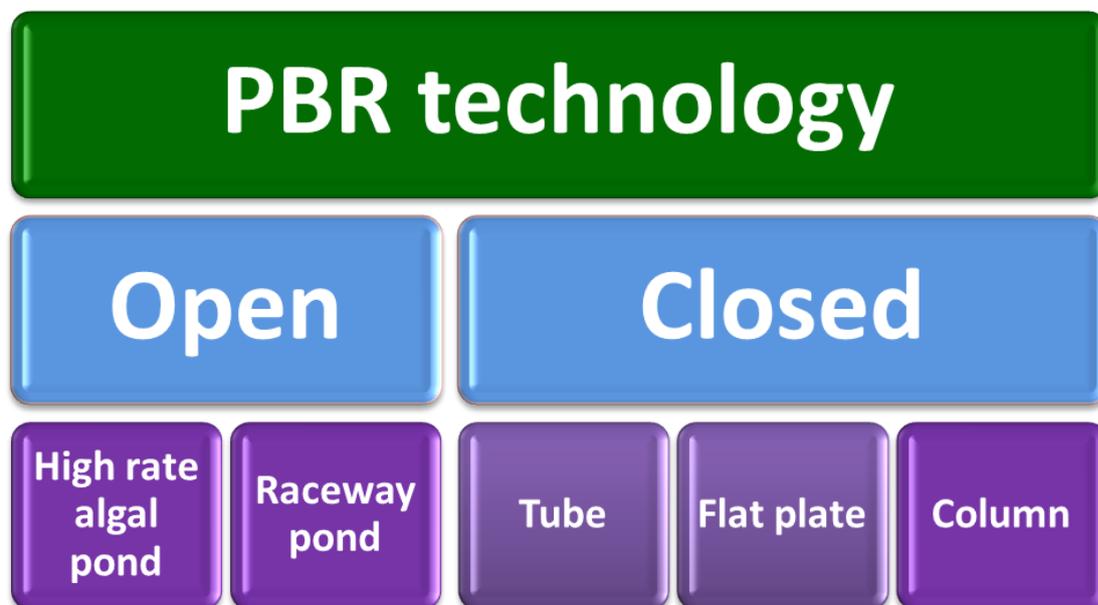
Figure 4:   Algal PBR system configurations

2   Carbon capture

The retention of carbon dioxide in a reactor is dependent on (a) mass transfer of the CO_2 from the gas to liquid phase and (b) assimilation of the CO_2 by the algae, with either one or both of these parameters being a function of the light intensity, CO_2 loading, biomass concentration and volume, biomass retention time, algal species, and solution chemistry (and specifically the pH and temperature). The system therefore has numerous variables, and individual experimental studies have not always provided all the relevant system parameter values.

Studies where a mass balance has been conducted (e.g. Chiang et al, 2011) indicate that most of the CO_2 uptake is assimilated as algal cells rather than unbound organics or extracellular polymeric substances. As a result, CO_2 uptake is generally determined solely from biomass generation through biochemical stoichiometry (Section 2.3), rather than through determination of CO_2 mass flow across the system. CO_2 uptake as a proportion of the supplied CO_2 is largely dependent on algal growth rate, such that in practice there is requirement for sufficient reactor capacity (in terms of the overall CO_2 retention time) for CO_2 assimilation. Many studies are based on single, bench-scale reactors of a few 100 mL volume (e.g. Tang et al, 2011), such that only a small percentage of the CO_2 is removed. However, studies conducted on larger-scale batch systems where the volume provided is sufficient for more significant capture, either for large sealed systems (Li et al, 2013) multi-stage reactors (Lam and Lee, 2013; Cheng et al, 2013) and/or reactors with recycle flows (Lam and Lee, 2013), suggest that high removals are attainable (Table 2). There is nonetheless currently a general paucity of pilot and demonstration

scale programmes exploring the most encouraging of the bench-scale findings regarding the most promising of the algal strains identified at bench scale with minimal overall % CO_2 removal.

Table 2 indicates that biomass production is generally in the range 0.26 to 0.7 g L^{-1} d^{-1} for moderate to high (2-20%) feed gas CO_2 concentrations. Applying a mass ratio of 1.9:1 CO_2:biomass carbon (Section 2.4) implies that the percentage carbon dioxide fixed in the biomass for operation at room temperature is given by:

$$\%F = 100\% \times 110PV/(CQ) = 100\% \times 110P\tau/C \qquad [1]$$

where P is the biomass productivity in g L^{-1} d^{-1}, V is the operating reactor volume, C is the %CO_2 in the feed gas stream, Q the gas flow rate in L d^{-1} and τ the gas residence time in days. Thus, for 100% removal, a moderate-to-high productivity of 0.5 g L^{-1} d^{-1} (Table 3) and a feed CO_2 concentration of 10%, τ = 10/(110 x 0.5) = 0.18 d, or 4.4 hours. Productivity is also a function of feed gas CO_2 concentration, though trends do not appear to be consistent across all studies (Table 2).

Table 2: Calculated and reported CO_2 fixation data, 2010 onwards

Algal species	C_{CO2} %	Q_g, mL/min	P, g/L/d	V, L	% CO_2 fixed	Note	Ref
Scenedesmus obliquus	10	200	0.29	0.2	0.002		Tang et al, 2011
Chlorella pyrenoidosa	10	200	0.26	0.2	0.002		Tang et al, 2011
Chlorella vulgaris	5		0.16-0.8	25	2-12	1	Lam & Lee, 2013
Chlorella PY-ZU1	15	30	0.95	0.3-4.2	2-86	3	Cheng et al, 2013
Chlorella vulgaris	15	25-50	0.24-0.35	8	36-56	2	Li et al, 2013
Scenedesmus sp.	10.6	100,000	0.43	20,000	66	4	De Godos et al, 2014
Botryococcus braunni	5	n.a.	0.50	8	88		Sydney et al, 2010
Chlorella vulgaris	5	n.a.	0.25	8	87		Sydney et al, 2010
Dunaliela tertiolecta	10	n.a.	0.27	8	80		Sydney et al, 2010
Anabaena sp.	5-15	*0.04**	0.65-0.8	5	90		Chiang et al, 2011
Spirulina platensis	2.5	200	0.99	1	n.a	5	Chen et al, 2013

C_{CO2} %CO_2 in feed gas; P Biomass production rate; Q_g Feed gas flow rate; V Reactor volume; *% CO_2 fixed* $100(1-C_{CO2out}/C_{CO2in})$. *vvm –volume of gas flow per minute per volume of liquid*

Notes
1. multi-stage w. recycle
2. closed raceway pond
3. multi-stage
4. raceway pond, 100 m^2, 0.4m deep
5. flat-type photobioreactor

Options for enhancing process intensivity include increasing light intensity, enhancing mass transfer and adjusting the chemical conditions. These are each considered in turn below.

2.1 Light intensity

Data for CO_2 fixation associated with specific light intensities, as provided by a number of authors for a range of algal species, is somewhat varied (Fig. 5). The data reveals no overall pattern between CO_2 fixation rates and light intensity either across different algal species or across different studies for the same algal species (e.g. *Chlorella vulgaris* or *Anabaena sp.*). On the other hand, within individual studies under the same controlled conditions (Table 3) it is evident that there is the expected increase in fixation and biomass productivity with light intensity and/or exposure, until reaching a maximum associated with light saturation (Chiang et al, 2011; Sánchez-Fernández et al, 2012; Ho et al, 2012; Gonçalves et al, 2014). Batch tests

conducted on four different algal species (*C. vulgari*, *P. subcapitata*, *S. salina*, and *M. aeruginosa*) suggest that an approximate trebling of light intensity (from 36 µmol m^{-2} s^{-1}) provides a 70-90% increase in growth rate and a 35-45% increase in biomass productivity and CO_2 uptake (Gonçalves et al, 2014). However, further increases in light intensity may then inhibit and diminish the CO_2 fixation rate and biomass productivity (Ho et al, 2012).
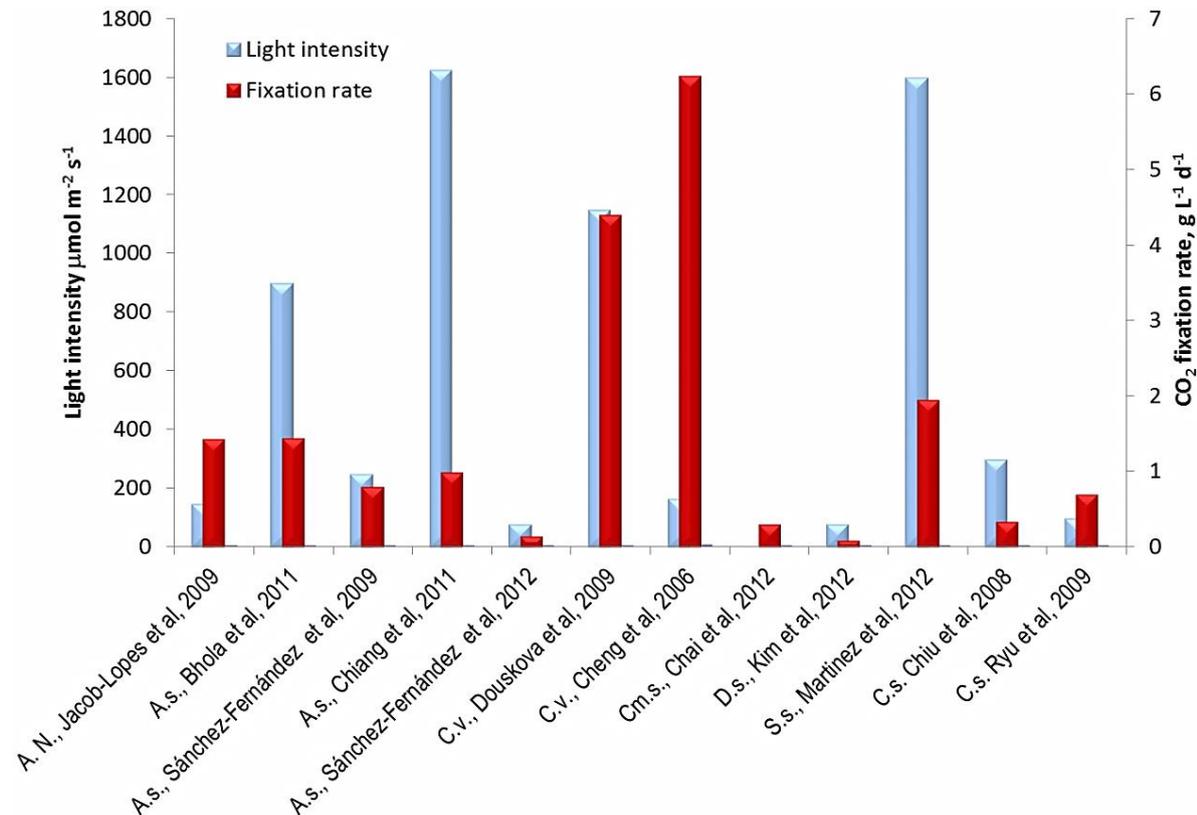
Figure 5:   Reported CO_2 fixation rates for various algal species (A.N. *Aphanothece microscopica Nägeli*, A.s. *Anabaena sp.*, C.v. *Chlorella vulgaris*, Cm.s. *Chlorococcum sp.*, D.s. *Dunaliella salina*, S.s. *Synechocystis sp.*, C.s. *Chlorella sp.*

Table 3:   Reported CO_2 fixation rates, Anabaena sp.

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}	Refs
900	1.45	2-3	3	0.03*	0.2	0.48	Sánchez-Fernández et al, 2009
0-460	0.43	3.3	0.76	10.6	~3 x 10^{-4}	~1	De Godos et al, 2014
250	0.65-0.8	5	0.58-1.2	5-15, 10	0.04	0.67-1.12	Chiang et al, 2011
650	0.16-0.58	0.7-6	0.35-0.95	0.03*	0.13-0.75	0.17-1.7	Sánchez-Fernández et al, 2012
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	

*atmospheric level; HRT = hydraulic residence time; vvm = volume gas per volume liquid per minute.

2.2   *Hydraulic residence time (HRT) and loading*

Quantitative trends in CO_2 uptake and associated productivity for continuous reactors are highly dependent on both the HRT and CO_2 loading. Decreasing the HRT, whilst detrimental to the biomass concentration, has nonetheless been shown to produce a maximum in CO_2 fixation rate and biomass productivity (Sánchez-Fernández et al, 2012) whilst generally being detrimental to removal of liquid-based contaminants such as nutrients (Section 3). Similarly, the percentage

CO_2 fixation appears to reach a maximum with CO_2 specific loading (i.e. the mass flow rate of CO_2) when loading is changed either by increasing the flow rate (Kargupta et al, 2015) or feed concentration (Chiang et al, 2011), according to batch reactor studies. Since this trend has been reported for three different species (*Chlorella pyrenoidosa* and *Scenedesmus abundans* by Kargupta et al, and *Anabaena sp.* by Chiang et al), it is apparently independent of microbiology and instead must presumably relate to some physicochemical facet of the system.

However, it is rare that all process parameter values influencing CO_2 capture have been reported. Many studies are based on batch systems, such that the impacts of the harvesting of the algae product and/or the recovery of the water are not evident, yet it has been demonstrated that the HRT impacts on CO_2 uptake (Sánchez-Fernández et al, 2012). Similarly, batch operation implies that steady-state conditions are not always reached, which has possible implications regarding the overall biochemical and chemical stoichiometry and specifically the pH-dependent carbonate equilibria (Section 2.4).

2.3   Mass transfer

Reported mass transfer coefficient (k_La) values for recent studies (Table 4) vary significantly, as expected, according to the system hydrodynamics. Whilst CO_2 uptake has been reported to increase with increased mass transfer coefficient (Fan et al, 2008), it is unclear as to whether a full-scale process is likely to be mass transfer limited, given the length of the total CO_2-liquid contact time required for biomass growth. Mass transfer is more critical in conventional aerobic treatment, of industrial wastewaters in particular, due to the higher carbon loads and the lower oxygen solubility compared with CO_2.

Table 4:   Reported mass transfer values for PBRs

Reactor configuration	k_La, h^{-1}	Reference
External loop airlift	17-24	Pirouzi Bioch et al, 2014
Membrane-sparged tubular reactor	250-430	Fan et al, 2008
Coarse bubble sparged reactor	20-65	Fan et al, 2008
Membrane contactor reactor	2.5-30	Fan et al, 2008
Tube	18	Fernández et al, 2012
Column	up to 23	Cervantes et al, 2013
Raceway pond	up to 9.6	Li et al, 2013

2.4   Biochemical and chemical stoichiometry

The general chemical formula of biomass, $CO_mH_nN_oP_p$, takes values of 0.242-0.485, 1.65-2.11, and 0.110-0.159 for m, n and o respectively, with p being around 0.1 for algal biomass (Tsygankov et al, 2002; Cheng et al, 2006; Ho et al, 2011; Chiang et al, 2011; Concas et al., 2012; Zhao and Su, 2014). There is then a 1:1 stoichiometic ratio of CO_2 carbon to algal carbon. Values of m-p appear to be comparable with those for biomass associated municipal wastewater treatment (Fig. 6). However, with wastewater treatment a complete carbon mass balance can be conducted by comparing the decrease in organic carbon substrate expressed as biochemical or chemical oxygen demand (BOD and COD) across the system with the increase in biomass generated. For algal bioreactors a mass balance can only be achieved by monitoring the inlet and outlet CO_2 concentrations. Whilst this has been conducted by some authors (Jacob-Lopes et al, 2010; Chiang et al, 2011; Kargupta et al, 2015) it is more usual for CO_2 fixation to be inferred from biomass production alone on the basis of, according to data in Fig. 6, the carbon contributing ~50% of the biomass by weight. From the 1:1 stoichiometry, this infers a weight ratio of ~2:1 CO_2:biomass, with a value of 1.88 often chosen (Chisti, 2007). Against this, a review of reported algal carbon content by Van Den Hende et al (2012) conducted across a

number of different genera revealed this parameter to vary between 36% for *Dunaliella tertiolecta* (Sydney et al, 2010) to 65% (Chae et al, 2006) for *Euglena gracilis*.
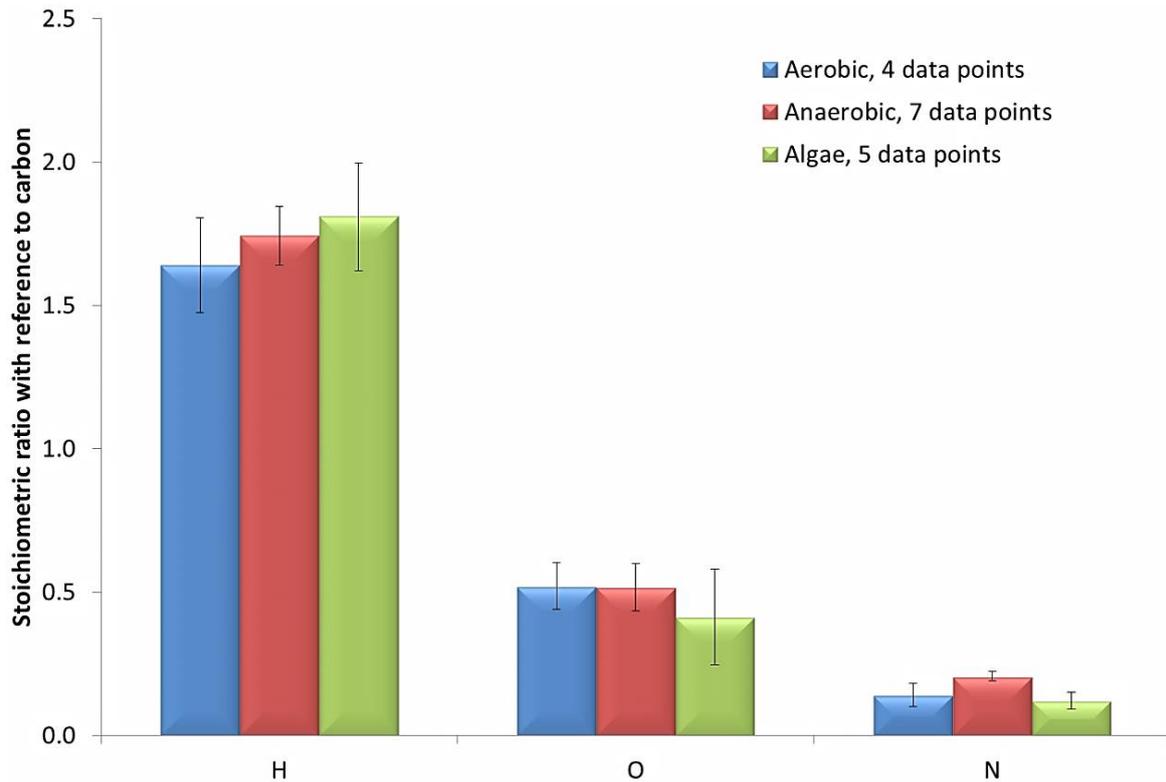
Figure 6:   Stoichiometric ratios of elements in biomass, averaged values from published data (Rittmann and McCarthy, 2001; Tsygankov et al, 2002; Cheng et al, 2006; Ho et al, 2011; Chiang et al, 2011; Concas et al., 2012; Zhao and Su, 2014)

Determining CO_2 uptake from biochemical stoichiometry is acceptable provided that the assumed biostoichiometry applies and that the net loss is entirely by assimilation. CO_2 dissolution or desorption on the other hand is evidenced by a change in pH, as implied by carbonate equilibria (Brezonik and Arnold, 2011) wherein the pH changes with the carbon dioxide to bicarbonate (HCO_3^-) ratio in accordance with the equation:

$$pH = \log \frac{[HCO_3^-]}{[CO_2]} + 6.38 \qquad\qquad [3]$$

This then demands that pH is monitored to allow the distinction between CO_2 uptake by assimilation and by dissolution, particularly in batch systems for which it has been demonstrated (Lam and Lee, 2013; Kargupta et al, 2015) that the solution carbonate concentration impacts significantly on CO_2 uptake.

3   Nutrient abatement

Algal-based PBRs offer a direct alternative to classical BNR. Given that both are biological processes, the key contributing factors with reference to their respective efficacies are (a) % nutrient removal, (b) retention time, (c) specific energy demand, (d) waste generation, and (e) the requirement for ancillary operations or consumables. BNR is integrated with an aerobic process which provides organic carbon removal but demands significant energy for process aeration of the aerobic tank. The PBR process, on the other hand, provides carbon dioxide

sequestration and also added value through the end algal products, but COD removal may vary from >90% (Zhou et al, 2012a) to almost none (Arbib et al, 2013) depending largely on the food:microorganism (F:M) ratio. A full cost benefit analysis is therefore challenging and very sensitive to assumptions made concerning the algal biomass processing and end product value. On the other hand, comparisons can be made based solely on the wastewater treatment technology for continuous systems (including semi-continuous technologies such as the sequencing batch reactor, SBR).

There has been significant interest in the application of PBRs to nutrient abatement in recent years (Table 5) encompassing a variety of municipal wastewaters of various strengths, from secondary effluent (Gao et al, 2015; Arbib et al, 2013) to primary clarifier effluent (Sutherland et al, 2014a-d), and anaerobic digester supernatant (Lee et al, 2015; Zhou et al, 2012a,b). According to this data, the mean hydraulic retention time (HRT), when reported, generally ranges between 2 and 5 days largely irrespective of technology configuration. This compares to total HRTs in the region of 7-15 hours (Table 6) for the BNR process, of which 30-70% is associated with the anaerobic (An) and anoxic (Ax) zones required for phosphorus (P) removal and denitrification (or nitrate removal) respectively. Nutrient removal is dependent on a number of parameters, including the nutrient balancing (the P:N:C ratio), the dissolved oxygen (DO) concentration in the different zones, the pH, and the temperature. Whilst these parameters have been widely explored for the BNR process, the key parameter of nutrient balancing appears to have largely overlooked in PBRs but has been shown to significantly increase N removal (Michels et al, 2014).

Algal PBR performance in terms of N and P removal appears comparable with that of the classical BNR process for a fully optimised process. However, ranges reported are much more scattered for the PBR process, with N and P removals as low as 47% and 12% N and P removal respectively reported (Table 5) compared with corresponding values of 73% and 67% for the BNR process (Table 6). For the most germane direct comparison between the BNR (Vaiopoulou and Aivasidis, 2008; Puig et al, 2008; Liu et al, 2008) and the HRAP (Sutherland et al 2014a-d) suspended growth processes challenged with municipal wastewater, the respective removal ranges are 73-87% N / 67-98% P for the BNR vs. 59-79% N / 12-79% P for the HRAP. The corresponding HRT values are 6.6-15 hours vs. 2-9 days. The algal process is therefore up to 15 times slower and is less robust in removing nutrient than the classical BNR one. Morever, a classical BNR plant employs a tank depth of ~5 m, compared to <0.5 m for a high-rate algal pond (HRAP). Overall, there is thus a two orders of magnitude difference in footprint between the BNR and PBR technologies.

Table 5: PBR nutrient removal papers from 2012 onwards, predominantly continuous systems

Species	Wastewater (municipal)	Technology	SS, g/L	Product-ivity g/m3/d	TP$_{in}$ mgL^{-1}	TN$_{in}$ mgL^{-1}	TP$_{out}$ mgL^{-1}	TN$_{out}$ mgL^{-1}	%N rem	%P rem	HRT, d	Reference	NB
S.c.	Secondary	Tub A-L	0.6-0.8	18-21	1.6-2.3	24-29	0.1-0.5	0.2-4	86-95	69-94	5	Arbib et al, 2013	
S.c.	Secondary	HRAP	0.2-0.3	5-8	1.6-2.3	24-29	0.5-1.1	5-12	62-77	51-63	10	Arbib et al, 2013	
C.v.	Secondary, anal.	BMPBR	1.37	72	0.8	15	0.35 ± 0.02	2.6 ± 0.6	83 ± 4	86 ± 2	2	Gao et al, 2015	
C.v.	Secondary, anal.	MPBR	0.95	50	0.8	15	0.34 ± 0.01	5.3 ± 1.0	64 ± 6	85 ± 3	2	Gao et al, 2015	
-	Primary, settled	HRAP	0.10-0.26^a	15-48	0.9-3.6	*20-31*	0.7-2.1	*4-14*	*47-79*	20-49	5.5-9	Sutherland et al, 2014a	a
P.b., D.o.	Primary, settled	HRAP	0.27	nr	4 ± 0.2	35 ± 5	2.9-3.4	12-15	56-67	15-28	2	Sutherland et al, 2014b	b
M.p.	Primary, settled	HRAP	0.18-0.23	14-17	3.2-6.3	*20-40*	0.7-2.7	*5-12*	74-75	58-79	4	Sutherland et al, 2014c	
M.p.	Primary, settled	HRAP	0.095-0.19	nr	4.6-7.2	*35-54*	-	-	*59-79*	12-34	4-9	Sutherland et al, 2014d	
-	Primary, settled	Biofilm	~0.3	2 ± 1 ^{b}	7 ± 3	66±16	1.1-1.7	13-25	70±8	85±9	3.1-5.2	Posadas et al, 2013	c
C.p.	Primary, settled	P. plate	0.35-0.8	42-60	8	*56*	-	-	*72*	92	0.64	Ramos Tercero et al, 2014	
C.v.	Anal.	Col MPBR	0.2-0.75	60 max	1.7-2.2	7.5-22	-	-	*>95 max*	>95 max	2-5	Marbelia et al, 2014	d
C.v.	Anal.	Col	0.2 max	33 max	1.7-2.2	7.5-22	-	-	*~85 max*	>95 max	5	Marbelia et al, 2014	e
T.s.	Fish farm eff.	Tube, batch	0.5	350	5	41	-	-	49	99	-	Michels et al, 2014	
O.m.,S.c.,C.v.	Tertiary	Batch	0.29-0.31	-	-	-	-	-	>99 max	>99 max	>4d	Ji et al, 2013	
A.p.	AD supernatant	Batch	2.5	-	-	-	-	-	69-74	25-75	-	Zhou et al, 2012a	f

refers to ammonia-N rather than TN

[a] Seasonally dependent pond organic matter: highest concentration in summer, lowest in winter: 7-18 deg C temperature range. % removal decreases with increasing load

[b] pH dependency of P removal

[c] units of g m^{-2} d^{-1}, i.e. with reference to biofilm area rather than reactor volume; 0.4-1.7 and 0.1-0.34 g m^{-2} d^{-1} of N and P loading respectively

[d] MPBR: N removal decreases from >95% to ~30% (P rem from ~95 to 50) as HRT decreases from 5 to 2 days; max productivity of 60 at 2 days HRT

[e] PBR: N removal decreases from ~85% to ~75% (P rem from 95% to 35%) as HRT decreases from 5 to 2 days; max productivity of 33 at 5 days HRT

[f] Removal loading-dependent.

KEY

Species		**Feedwater**	
A.p.	*Auxenochlorella protothecoides*	AD	anaerobic digester
C.a.	*Coelastrum*	Anal.	analogue
C.k.	*Chlorella kessleri*	**Reactor configuration**	
C.p.	*Chlorella protothecoides*	BMPBR	biofilm membrane bioreactor
C.v.	*Chlorella vulgaris*	Col	column
D.o.	*Desmodesmus opoliensis*	HRAP	high-rate algal ponds
M.p.	*Mucidosphaerium pulchellum*	MPBR	membrane photobioreactor
O.m.	*O. multisporus*	P. plate	parallel plate
P.b.	*Pediastrum boryanum*	Tub A-L	tubular air-lift
S.c.	*Scenedesmus obliquus*		
T.s.	*Tetraselmis suecica*		

Table 6:   BNR papers, municipal wastewater

Feed	Hydraulic residence time, h				% Nutrient removal		Notes	Ref
	An	Ax	Ae	Total	N	P		
Real	5.4	1.35	2.25	9	73	67	Mean removals	Vaiopoulou & Aivasidis, 2008
Analogue	2	4	8	14	83-88	68-80	Combined optimum	Brown et al, 2011
Analogue	2	2	4	8	90	99	Optimum	Liu et al, 2013
Real	-	3.1-4.6	6-9	9.3-15	75	98	Optimum	Zeng et al, 2011
Real	1.8	2.6	2.2	6.6	87	94	Optimum	Puig et al, 2008
Analogue	3	3	3	9	73-77	87-95	pH dependent	Liu et al, 2008

The reduced robustness compared with the BNR process arises primarily from the combined impact of the lower biomass concentration (generally below 1.5 g/L, Table 3) compared with the BNR process (>3 g/L, and between 8 and 15 g/L for a membrane bioreactor, Judd, 2014) combined with the concomitant slower biokinetics of the algal system. Against this, very high removals (>99%) and/or reduced HRTs (16 h) have been reported for the "advanced" PBR process configurations of column (Marbelia et al, 2014) and parallel plate biofilm (Ramos et al, 2014) reactors respectively, with further HRT reductions (<8 h) apparently achievable using immobilised systems (Filippino et al, 2015). Removal is otherwise also sensitive to the pH swings associated with CO_2 hydrolysis (Section 2.4), since adsorption of inorganic phosphates is possible at pH values above 8 (Song et al, 2002; Zhou et al 2012b; Sutherland et al, 2014b). Nutrient removal efficiencies also decrease with increasing feed concentrations (Ramos Tacero et al, 2014; Sutherland et al, 2014c) and with decreasing HRT, due to the limited nutrient uptake rate of the algal biomass. For example, a maximum uptake rate of ~4-5 mg/L/d N and 0.4-0.6 mg/L/d P has been reported for both a classical stirred tank PBR and a membrane PBR operating at a 2-5 d HRT (Marbelia et al, 2014).

The apparently inferior performance of the PBR over classical BNR is nonetheless to a large extent mitigated by the reduced energy demand and the in-situ photosynthetic oxygenation provided by microalgae, which can support the microbial oxidation of recalcitrant and toxic organic contaminants and reduce the costs associated with conventional mechanical aeration in conventional activated sludge systems. This in-situ O_2 production serves to provide a treated effluent with an elevated dissolved oxygen concentration. Algae also permit augmentation of P removal through its accumulation within algal cells as polyphosphate (known as "luxury" uptake, Brown and Shilton, 2014).

Combined biofuel and nutrient recovery from the algal biomass has been demonstrated through established processes such as hydrothermal liquefaction. The latter has been shown to recover ~60 wt% of the original algae protein content as ammonium and nitrate ions and protein/polypeptides (Sunphorka et al, 2014). Nutrient recovery *per se* is likely to be increasingly economically viable in the future, particularly in the case of phosphate for which the global reserves are finite (Keeley et al, 2012). The lower energy demand and process simplicity of PBRs, which unlike the BNR process demand no aeration or multiple zones of differing biochemical potential, are perhaps the primary motivating factors for the proliferation of recent research publications in the area.

4   Conclusions

The combined carbon dioxide capture/fixation from gaseous discharges and nutrient removal of from wastewater sources presents a significant opportunity for algal photobioreactor (PBR) technology. An examination of published data in this area indicates:

a) a dramatic increase in publication rate in this area since ~2007;

b) a focus primarily on growth rate determination at bench scale of a range of candidate algal species;

c) algal growth rates of around 0.5 g L^{-1} d^{-1}, with operating steady-state biomass concentrations generally below 1 g L^{-1}, demanding a CO_2 gas residence time of over four hours for its complete fixation from a feed gas containing 10% CO_2;

d) hydraulic residence times (HRTs) of 2-5 days for up to 80% nutrient removal for a classical high rate algal PBR (HRAP), compared to values of around 12 hours for a classical biological nutrient removal (BNR) process, contributing to an increased footprint of two orders of magnitude for the HRAP.

The combined carbon capture/nutrient removal process is challenged by requirement to balance loads of both carbon and nutrient from the two different process streams (gas and aqueous, both of which contain both carbon and nutrient sources) to sustain the system biology. Process optimisation on the basis of CO_2 capture and biomass growth does not necessarily follow that for nutrient removal. There is evidently a profound impact of algal speciation on system performance, as manifested by widely varying CO_2 fixation and nutrient removal values, and the process itself is powered by light whose intensity also influences the process efficiency. The carbon dissolution and hydrolysis solution chemistry and temperature also impacts on the process. There are thus key synergistic relationships between many of the process design and operational parameters (principally microalgal strain, C:N:P load and balance, CO_2 and liquid residence time, light intensity and quality, temperature, and reactor configuration) which impose a significant challenge to the overall process control and which have yet to be fully explored. The complexity of the system suggests that the use of statistical experimental planning may be beneficial in allowing all key variables to be encompassed and their synergies evaluated for system optimisation.

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