Modelling and Evaluation of CO₂ Supply and Utilisation in Algal Ponds

Aidong Yang

Division of Civil, Chemical, and Environmental Engineering, Faculty of Engineering and Physical Sciences,
University of Surrey, Guildford, UK

Email: a.yang@surrey.ac.uk

Abstract: A mathematical model was constructed to simulate the behaviour of an open algal pond particularly with respect to CO₂ supply and utilisation. The algal pond considered takes wastewater as feed, which provides substrate for aerobic bacteria and also nutrients for the algal-bacterial consortium. CO₂-containing gas such as flue gas or biogas is considered as additional source of CO₂ to support the growth of algae which at the same time also serves the purpose of CO₂ abatement. A number of simulation studies were carried out to evaluate the performance of the system in terms of the production of algae, treatment of wastewater, and CO₂ fixation and removal. Important design and operating parameters were considered, including pond depth, hydraulic retention time, composition of the feed wastewater, flowrate and CO₂ fraction of the supplied gas flow, and the area utilised for gas flow induction. Several useful observations were made based on the simulation results, with the potential to provide guidance to the future practical development of multi-functional algal ponds.

Keywords: Microalgae; algal pond; mathematical modelling; wastewater treatment; CO₂ capture

1. Introduction

Recent concerns on climate change and depletion of fossil feedstock have demanded the utilisation of renewable resources, including particularly biomass, to enable sustainable production of energy, chemicals and materials. In this context, microalgae as an important type of aquatic biomass are receiving significant attention, due to their potential of producing renewable energy and chemicals through photosynthesis in a way more efficient than many terrestrial plants¹.

Microalgae can be artificially grown in photobioreactors (PBRs) where light is applied to the culture medium which contains nutrients and CO₂, to enable the photosynthesis process. Two main types of PBRs can be distinguished, namely open ponds and closed reactors². In comparison with open ponds, it is widely agreed that closed PBRs potentially can achieve higher biomass productivity and are easier to control particularly with respect to the avoidance of contamination³. A number of PBR designs have been studied so far; see [3] and [4] for a review of the development in this area. However, despite the technical advantages of closed PBRs, they currently suffer from capital and operating costs which are considerably higher than open ponds. Consequently, open ponds are still considered as a more practical option particularly for large scale cultivation.

The growth of algae requires the supply of nutrients and CO₂ in addition to light. When the supply is made from a purposefully manufactured source, this not only adds to the operating cost but also reduces the life-cycle environmental benefit of the otherwise promising algal system due to the energy and raw material consumptions and GHG (greenhouse gas) emissions in the process of producing these supplies⁵. To circumvent these problems, a popular idea has been growing algae in nutrient-rich wastewater and with unwanted CO₂ that is present in e.g. flue gas generated in combustion processes^{6,7,8}. With such arrangements, the purposefully manufactured supply of nutrients and CO₂ may be completely avoided or reduced to a certain extent. Additionally, such a system will possess functions of treating wastewater and removal of CO₂ from industrial emissions, in addition to the production of valuable algal biomass.

The above idea has been examined in a number of experimental investigations. In a wastewater treatment system termed “advanced integrated wastewater pond system”^{9,10,11}, anaerobic digestion (AD) takes place in a pit located at the bottom of a facultative pond, where biogas produced by the AD pit is scrubbed by the water column when it rises to the pond surface. This pond is followed by a so-called High Rate Algal Pond (HRAP), where algae grow in the AD effluent in symbiosis with aerobic bacteria. The bacteria digest organic compounds with oxygen produced by the photosynthesising algae which in turn consume CO₂ produced by the bacteria, in addition to some more subtle relations between these two microbial populations¹². Several more recent studies have experimentally investigated HRAPs as standalone systems;

benefits (in terms of algal biomass yield and waste water treatment performance) of supplying CO_2 into the system in addition to that available from the atmosphere were reported^{13,14,15}.

From these existing investigations, it is evident that CO_2 supply and utilisation is an important aspect of growing algae in wastewater with CO_2 sparging. However, this aspect is still to be systematically understood. For example, the effect of CO_2 sparging at different flowrates and CO_2 concentrations has not been analysed in detail in the past. The relationship between bacterial oxidation, algal photosynthesis, and supply of additional CO_2 is still to be examined, too.

The objective of this work has been to develop a mathematical model and use it to evaluate the impact of the important design and operating parameters that affect CO_2 supply and utilisation in an HRAP-type algal pond. In the rest of the paper, the key characteristics of the assumed algal pond are outlined in Section 2. Section 3 presents the mathematical model. In Section 4, the design of simulation runs for evaluating the behaviour and performance of the system is described. Simulation results are presented in Section 5 with discussions on biomass production, wastewater treatment and CO_2 abatement, before conclusions are drawn in Section 6.

2. Description of the assumed algal pond

The type of algal pond considered in this work is schematically shown in Figure 1.

Figure 1. Schematic of the algal pond.

In addition to sun light, the input to the pond includes the following:

Influent wastewater: The content of the wastewater is characterised by Biological Oxygen Demand (BOD), total inorganic carbon (with species including dissolved free CO_2 , HCO_3^- , and CO_3^{2-}) and total ammonium nitrogen (including NH_4^+ and NH_3). As well as participating to the metabolism of the microbial consortium in the pond, the latter two are also important for determining the pH in the system. Other nutrients such as phosphorus are not explicitly considered, with the assumption that the metabolism of the microbial consortium are not limited or inhibited by those compounds and that their removal can be quantified in a way similar to that of nitrogen (i.e. by following the corresponding stoichiometry, cf. Section 3.2).

Gas flow that contains CO_2 : Two cases can be distinguished. In the first case, a gas flow contains CO_2 which is to be fixed into algal biomass, either completely or partially; flue gas from a combustion process is a typical example. In the second case, the gas flow is to be cleaned by removing CO_2 from this flow; the removed CO_2 may be fixed into algal biomass or leave the system through other outlets. An example of the second case is the purification of biogas generated in an anaerobic digestion process. In the sequel, these two cases will be referred to as *CO_2 fixation* and *CO_2 removal*, respectively. For both cases, the sparging of gas is modelled in the same way, assuming that it takes place at the bottom of part of or the whole pond through orifices, similar to the approach assumed by Shang et al. for studying heat supply to algal ponds through waste gas flows¹⁶. This current work assumes a constant temperature of the pond (20°C) and focuses on the supply of CO_2 only. Other approaches for CO_2 sparging are not evaluated but will be briefly discussed in Section 5.3.

The outlets of the system include effluent water flow, effluent gas flow, and algal and bacterial biomass. Some kind of effluent gas capture or collection would be required for the case of CO_2 removal. However, no specific design of such a device is considered in this work. The separation of algal biomass is not considered either. Additionally, there can be exchange of CO_2 and O_2 between the pond and the atmosphere; the direction of flow depends on the concentration of the dissolved gases in the pond.

Inside the pond lives the algal-bacterial consortium. The interactions between these two parties as considered in this work include the transfer of oxygen generated by the photosynthesising algae to the bacteria and that of CO₂ produced in the oxidation process by the bacteria to algae.

With regard to the design and hydrodynamics of the pond, a reference is made to the typical configuration of HRAPs where a race-way type of flow channel layout is frequently adopted together with a paddle wheel type of device for creating the flow in the pond¹⁷. Furthermore, the liquid content of the pond is assumed to have a constant volume (denoted as the pond volume), and no water loss or gain due to evaporation or precipitation is considered.

3. The mathematical model

There are three aspects of the algal pond to be considered for setting up a mathematical model of the system. These are addressed in the following subsections.

3.1 Flow and mixing

An approach reported in the literature^{18,19} was adopted here which uses a number of serially connected completely-mixed stirred reactors (CSTRs) with a recirculation loop to approximate race-way type of hydrodynamics of the algal pond which often exhibits a certain degree of heterogeneity along the flow in the race-way channel. According to Buhr and Miller¹⁸, a configuration of about 10-25 well mixed reactors with a properly set recirculation flowrate is able to render a satisfactory approximation. For a given effluent water flowrate, the total volume of the pond is determined by the hydraulic retention time (HRT). The total surface area is in turn related to the total volume via the depth of the pond. The composition of a flow that connects two neighbouring CSTRs is same as that of the fluid in the upstream CSTR. The flow rate of the recirculation flow leaving the last CSTR and entering the first CSTR in the series is determined by the volume of the pond and the recirculation time as specified in the pond design. Between other neighbouring CSTRs, the flow rate is the sum of the flow rate of the feed stream of the whole pond and that of the recirculation flow.

3.2 Algal-bacterial consortium

The behaviour of the algal-bacterial consortium is modelled considering a well mixed reactor as part of the series of reactors mentioned above. A few models for such a system were proposed in the past^{18,21-24}. The current work has adopted the model developed by Buhr and Millar¹⁸. In comparison with other models, this model offers a clear approach to the estimation of pH, which is important for establishing the inorganic carbon balance in the system²⁴. Furthermore, this model was originally validated against experimental data; good agreement was observed between simulated and measured quantities such as dissolved oxygen and pH.

Kinetics and mass balance of algae

The growth rate of algae is modelled by Eq. (1):

$$r_{gA} = \mu_A X_A, \quad (1)$$

where μ_A and X_A are the specific growth rate and mass concentration of algae, respectively. The specific growth rate of algae is affected by dissolved CO₂ (CO_{2D}), total nitrogen (N_T), as well as light intensity, as expressed in Eq. (2):

$$\mu_A = \hat{\mu}_A \left(\frac{CO_{2D}}{K_c + CO_{2D}} \right) \left(\frac{N_T}{K_{NA} + N_T} \right) f_I, \quad (2)$$

$\hat{\mu}_A$, K_c , and K_{NA} are constants. f_I , the light intensity factor, is modelled by the following equation³⁵:

$$f_I = \frac{I_a}{I_s} \exp\left(1 - \frac{I_a}{I_s}\right), \quad (3)$$

where I_s is the saturation light intensity, I_a is the (spatial) average light intensity in the pond at a particular point in time. Following Beer Lambert's law, I_a can be estimated as follows:

$$I_a = \frac{1}{Z} \int_0^Z I_0 \exp(-K_e z) dz, \quad (4a)$$

where I_0 is the surface light intensity, K_e is the extinction coefficient, Z is the depth of the pond. K_e is correlated to algal concentration in the pond (X_A) by¹⁹:

$$K_e = K_{e1} + K_{e2} X_A, \quad (4b)$$

where K_{e1} and K_{e2} are constants. The diurnal variation of the surface light intensity, I_0 , can be approximated by a sinusoidal function for the photoperiod²⁵:

$$I_0(t) = \left(\frac{\pi I_d}{2 f_p}\right) \sin\left(\frac{\pi t}{f_p}\right), \quad (4c)$$

I_d is the daily total light intensity at pond surface, f_p is the fraction of the photoperiod in a day, t (unit: day) is the relative time in the photoperiod. Out of the photoperiod I_0 is zero. The specific values of I_d and f_p used in the simulation experiments are given later in Table 2.

The decay rate of algae is modelled by Eq. (5):

$$r_{dA} = k_{dA} X_A, \quad (5)$$

where k_{dA} is a constant. Considering further the algal content in the influent and the effluent, the mass balance of algae is expressed as

$$\frac{dX_A}{dt} = \frac{F}{V} (X_{A0} - X_A) + r_{gA} - r_{dA}, \quad (6)$$

F is the mass flowrate of the influent and effluent, V is the volume of the reactor, X_{A0} is the algal concentration in the influent.

Kinetics and mass balance of bacteria

The growth rate of bacteria is modelled by Eq. (7):

$$r_{gB} = \mu_B X_B, \quad (7)$$

where μ_B and X_B are the specific growth rate and mass concentration of bacteria, respectively. The specific growth rate is further modelled by Eq. (8):

$$\mu_B = \hat{\mu}_B \left(\frac{S}{K_S + S}\right) \left(\frac{O_2}{K_{O_2} + O_2}\right) \left(\frac{N_T}{K_{NB} + N_T}\right), \quad (8)$$

S is the concentration of the substrate (measured by BOD), $\hat{\mu}_B$, K_S , K_{O_2} , and K_{NB} are constants.

The decay rate of bacteria is modelled by Eq. (9):

$$r_{dB} = k_{dB} X_B, \quad (9)$$

where k_{dB} is a constant. Similar to that of algae, the mass balance of bacteria is expressed as

$$\frac{dX_B}{dt} = \frac{F}{V} (X_{B0} - X_B) + r_{gB} - r_{dB}, \quad (10)$$

X_{B0} is the bacterial concentration in the influent.

Balances of substrate, inorganic carbon, total nitrogen, and oxygen

The balance of these components is modelled by linking to the stoichiometry of algal and bacterial growth.

For substrate, the balance equation reads

$$\frac{dS}{dt} = \frac{F}{V}(S_0 - S) - \mu_B X_B Y_B, \quad (11)$$

S_0 is the substrate mass concentration in the influent, Y_B is the mass of substrate consumed per unit mass of bacteria produced.

The balance of total inorganic carbon, total (ammonium) nitrogen, and oxygen can be modelled in a very similar way:

$$\frac{dM}{dt} = \frac{F}{V}(M_0 - M) + \mu_B X_B Y_{BM} + \mu_A X_A Y_{AM} + f_g - k_{Lg} \alpha (M_g - M_g^*), \quad (12)$$

M represents the molar concentration of total inorganic carbon, total nitrogen, or oxygen. M_0 and M are the concentration of the respective component in the influent and effluent, respectively. $Y_{B,M}$ and $Y_{A,M}$ are the mass of the respective component consumed or generated per unit mass of bacteria and algae produced, respectively. Note particularly that the generation and consumption of O_2 and CO_2 (as a form of inorganic carbon) by algae and bacteria are all handled via these two variables. f_g represents the flux of the respective gases (with g denoting CO_2 , NH_3 , or O_2) introduced by the supply of gas flow into the system. The last term of the right hand side of Eq. (12), i.e. $k_{Lg} \alpha (M_g - M_g^*)$, represents the mass transfer between the atmosphere and the pond, where k_{Lg} , M_g , and M_g^* are mass transfer coefficient, concentration and saturation concentration of the respective dissolved gas. The saturation concentration for NH_3 is zero and those for CO_2 , and O_2 are estimated by Henry's law:

$$M_g^* = K_{Hg} P_g, \quad (13)$$

K_H and P are Henry's constant and partial pressure of the gas g in the atmosphere.

It should be noted that minor modifications to the balance equations (Eqs. 6, 10, 11, 12) are required for the first CSTR in the series which has the recirculation flow as an additional input (cf. Section 3.1).

Ionic equilibrium (pH estimation)

Applying the principles of solution equilibrium and charge neutrality, this aspect is modelled by the following equations¹⁸:

$$\left. \begin{aligned} NH_4^+ &= \frac{(N_T)(H^+)}{H^+ + K_A} \\ HCO_3^- &= \frac{NH_4^+ + Z}{1 + 2K_{2C}/H^+} \\ CO_{2D} &= \frac{(H^+)(HCO_3^-)}{K_{1C}} \\ CO_3^{2-} &= \frac{(HCO_3^-)(K_{2C})}{H^+} \end{aligned} \right\} \quad (14a)$$

Here Z represents the net concentration of all “inert” ions (i.e. those other than CO_3^{2-} , H^+ , HCO_3^- , NH_4^+ , and OH^-). N_T and C_T are total (ammonium) nitrogen and total inorganic carbon, respectively. Applying mass balance to the involved species gives

$$\left. \begin{aligned} N_T &= NH_4^+ + NH_3 \\ C_T &= CO_{2D} + HCO_3^- + CO_3^{2-} \end{aligned} \right\} \quad (14b)$$

K_A , K_{1C} , and K_{2C} in Eq. (14a) are equilibrium constants and can be evaluated as follows¹⁸:

$$\left. \begin{aligned} K_A &= 10^{(-pK_A + p\gamma_H - p\gamma_{NH_4})} \\ K_{1C} &= 10^{(-pK_{1C} + p\gamma_H + p\gamma_{HCO_3})} \\ K_{2C} &= 10^{(-pK_{2C} + p\gamma_H + p\gamma_{CO_3} - p\gamma_{NH_4})} \end{aligned} \right\} \quad (15)$$

where pK_A , pK_{1C} , and pK_{2C} are constants (with p representing negative logarithm). The negative logarithm of activity coefficients, $p\gamma$, can be calculated by¹⁸

$$p\gamma = G\zeta^2 \{ \sqrt{I} / (1 + aB\sqrt{I}) \}, \quad (16)$$

G , a , and B are all constants, ζ and I are ionic valency and ionic strength of the solution, respectively.

3.3 Gas bubbling and liquid-gas mass transfer

It is assumed that gas is supplied to the system at the bottom of one or more CSTRs through a certain gas distribution area composed of a number of orifices. The mass balance of CO₂ in the gas flow can be modelled as follows:

$$\frac{\partial CO_2}{\partial t} - u_{Gb} \frac{\partial CO_2}{\partial z} = k_{Lb} \alpha_b (CO_{2_d}^{b*} - CO_{2_d}), \quad (17)$$

CO₂ is the molar concentration of CO₂ in the bubble phase, u_{Gb} is the ascending velocity of bubbles, z represents the depth dimension, k_{Lb} and α_b are CO₂ mass transfer rate from the bubbles to the liquid phase and corresponding specific mass transfer area (i.e. bubble surface area per unit gas volume), $CO_{2_d}^{b*}$ is the saturation concentration of the dissolved CO₂ in the liquid phase in equilibrium with the CO₂ in the bubbles, and can be calculated using Henry's law (cf. Eq. (12)). The absorption of gases other than CO₂ can be considered in a similar way, which however is ignored in the present work.

Assuming bubbles are all equal-sized and spherical, specific mass transfer area is

$$\alpha_b = \frac{\pi d_b^2}{\frac{1}{6} \pi d_b^3} = \frac{6}{d_b}, \quad (18)$$

d_b is the diameter of bubbles. Assuming d_b remains constant, it can be estimated by¹⁶

$$\frac{d_b}{d_0} = 3.23 Re^{-0.1} Fr^{0.21} \quad (19)$$

d_0 is the diameter of orifices. Re and Fr are the Reynolds number and the Froude number:

$$Re = \frac{4Q_0}{\pi d_0 \mu_L} \quad (20)$$

$$Fr = \frac{Q_0^2}{d_0^5 g} \quad (21)$$

where ρ_L and μ_L are the density and dynamic viscosity of the liquid phase, Q_0 is the gas volumetric flowrate per orifice determined by the total volumetric flowrate (Q), number of orifices per unit area (n), and the total area utilised for introducing the gas flow (A_g):

$$Q_0 = \frac{Q}{nA_g} \cdot \quad (22)$$

To estimate the mass transfer coefficient k_{Lb} , the following correlation was adopted²⁶.

$$k_{Lb} = \frac{D_{CO_2} (2 + 0.015 (\frac{\rho_L u_{rel} d_b}{\mu_L})^{0.89} (\frac{\mu}{\rho D_{CO_2}})^{0.7})}{d_b}, \quad (23)$$

D_{CO_2} is the diffusivity of CO_2 in water, u_{rel} is the bubble-liquid relative velocity.

It was noticed that a number of alternative correlations were available for estimating the mass transfer coefficient in a bubble-column type of system²⁷. According to Maceiras et al.²⁸, the upper and lower values of the coefficient can be estimated by the following two equations, each with the assumption of surface mobility at one extreme:

$$k_L^{mobile} = 1.13 \sqrt{\frac{u_{rel}}{d_b}} D_{CO_2}^{1/2} \quad (24)$$

$$k_L^{rigid} = 0.6 \sqrt{\frac{u_{rel}}{d_b}} D_{CO_2}^{2/3} \left(\frac{\mu_L}{\rho_L} \right)^{-1/6} \quad (25)$$

In this work, the estimates by Eq. (23) were compared with the upper (k_L^{mobile}) and lower (k_L^{rigid}) values for a range of u_{rel} relevant to this current study. Figure 2 indicates that Eq. (23) appears to be a reasonable choice.

Figure 2. Comparison between different k_L estimates.

The application of this correlation requires the bubble-liquid relative velocity, which is approximated by the bubble ascending velocity u_{Gb} . u_{Gb} is estimated using the following correlation¹⁶:

$$u_{Gb} = \sqrt{\frac{4d_b g}{3C_D}}, \quad (26)$$

C_D , the drag force coefficient, is estimated by

$$C_D = \begin{cases} \frac{18.5}{\text{Re}^{0.6}} & \text{for } 1 < \text{Re} < 1000 \\ 0.44 & \text{for } \text{Re} \geq 1000 \end{cases} \quad (27)$$

The above model construction can now be linked to the term f_g in Eq. (12), or more specifically f_{CO_2} because the rate of CO_2 supply (per unit pond volume) is what is to be captured in this study:

$$f_g = \frac{1}{Z} \varepsilon \int_0^Z K_{Lb} \alpha_b (CO_{2_d}^{b*} - CO_{2_d}) dz, \quad (28)$$

The integrand is the right hand side of Eq. (17). Here Z is the depth of the pond, ε is the volume fraction of gas holdup and can be estimated by

$$\varepsilon = \frac{n \pi d_b^3 f}{6 u_{Gb}}, \quad (29)$$

where n is the number of orifices per unit area, f is the frequency for bubbles to occur at each orifice:

$$f = \frac{6Q_0}{\pi d_b^3}. \quad (30)$$

This completes the entire mathematical model of the algal pond to be simulated. The numerical values of the model parameters used in this study are given in Table 1.

Table 1. Numerical values of model parameters

Parameter	Value	Reference
$\hat{\mu}_A$	0.9991 days ⁻¹	[18]
$\hat{\mu}_B$	5.0432 days ⁻¹	
K_{H,CO_2}	39.7386 mol m ⁻³ atm ⁻¹	
K_{H,O_2}	1.4132 mol m ⁻³ atm ⁻¹	
pK_A	9.4003	
pK_{1C}	6.3819	
pK_{2C}	10.3767	
G	0.5072	
B	0.3282	
a	NH ₄ ⁺ = 3; HCO ₃ ⁻ = 4; CO ₃ ²⁻ = 5; H ⁺ =9	
Y_B	2.5 g BOD consumed (g bacterial mass produced) ⁻¹	
Y_{A,CO_2}	0.0496 mol CO ₂ consumed (g algal mass produced) ⁻¹	
Y_{A,O_2}	0.0496 mol O ₂ produced (g algal mass produced) ⁻¹	
$Y_{A,N}$	0.00652 mol N consumed (g algal mass produced) ⁻¹	
Y_{B,CO_2}	0.078 mol CO ₂ produced (g bacterial mass produced) ⁻¹	
Y_{B,O_2}	0.078 mol O ₂ consumed (g bacterial mass produced) ⁻¹	
$Y_{B,N}$	0.00885 mol N consumed (g bacterial mass produced) ⁻¹	
k_{dA}	0.05 days ⁻¹	
k_{dB}	0.10 days ⁻¹	
K_S	150 g BOD m ⁻³	
K_C	0.001 mol CO _{2D} m ⁻³	
K_{NA}, K_{NB}	0.001 mol N m ⁻³	
K_{O_2}	0.008 mol CO _{2D} m ⁻³	
P_{O_2}	0.21 atm	
P_{CO_2}	0.00032 atm	
K_{L,O_2}	0.24 m h ⁻¹	[29]
K_{L,CO_2}	$k_{L,O_2} (D_{CO_2}/D_{O_2})^{1/2}$	This work
K_{L,NH_3}	$k_{L,O_2} (D_{NH_3}/D_{O_2})^{1/2}$	This work

D_{CO_2}	1.97e-9 m ² /s	[30]
D_{NH_3}	1.94e-9 m ² /s	[30]
D_{O_2}	2.10e-9 m ² /s	[31]
K_{e1}	0.32 m ⁻¹	[19]
K_{e2}	0.03 m ⁻¹ (g/m ³) ⁻¹	[19]
I_s	14.63 MJ/m ² /day	Range of 8.36 to 20.9 MJ/m ² /day cited in [32]; an average taken by this work
ρ_L	1e3 kg/m ³	Approximate value for pure water
μ_L	9.07e-4 pa s	Value for pure water at 20°C ³⁶

4. Design of simulation experiments

A number of simulation experiments were carefully designed to investigate how design and operating parameters would affect the performance of the algal pond particularly in connection with CO₂ supply and utilisation.

4.1 Design and operating parameters

Table 2 lists the setting of the parameters in terms of the value for the base or nominal case and the range investigated in various simulation runs.

Table 2. Design and operating parameters of the algal pond adopted in simulation

	Parameter	Nominal value	Range
Pond	Pond depth (m)	0.4	0.1-0.4
	Hydraulic retention time (day)	7	5-10
	Recirculation time (hour)	1	-
	Temperature (°C)	20	-
	Number of CSTR (-)	20	-
	Surface light intensity (MJ/m ² /day)	18.81	
	Photoperiod (in a 24-hour day)	Hour 5 – Hour 19	
Influent wastewater	Influent wastewater flowrate (m ³ /day)	50	-
	Temperature (°C)	20	
	BOD (g/m ³)	300	0-600
	Total inorganic carbon (mol/m ³)	8.5	-
	Total ammonium nitrogen (mol/m ³)	5.0	-
	Oxygen (mol/m ³)	0.125	-
	Inert ions (mol/m ³)	3.5	-
Supplied gas	Flowrate (m ³ /hour)	10	0-50
	Pressure (MPa)	0.11	-
	Temperature (°C)	20	
	CO ₂ molar fraction (%)	10	10, 30
Gas induction	Orifice diameter (m)	0.05	-
	Number of orifices per m ² (-)	250	-
	Percentage of pond bottom area for gas induction (%)	100	5-100

The composition of the influent wastewater was set according to [18]. The diameter and number of orifices are the same as adopted in [16]. Although the above definitions were not exactly based on a specific physical prototype, the nominal case does refer to a possible algal pond that follows an anaerobic digestion unit, which generates effluent flow at 50m³/day and up to 50 m³/h biogas. These two flows may subsequently become the input to the algal pond discussed here. The lower and higher levels of CO₂ fractions were set to represent cases of flue gas and biogas, respectively.

4.2 Performance indicators

Several indicators were defined to quantify the performance of the algal pond. All indicators were calculated based on the simulation results characterising the cyclic steady state of the system which normally is reached after an initial transient period. These indicators include:

- Algal biomass productivity, denoted by the daily production of algae;
- BOD removal, denoted by the daily average concentration of BOD of the effluent of the pond;

- CO₂ fixation: The absolute amount of CO₂ “fixed” daily by the system, C_{fix} , equals to that consumed by algae. It should be noted that any CO₂ molecule fixed by algal growth may potentially come from one of the four different sources of inorganic carbon, namely the influent wastewater (C_{inf}), atmosphere (C_{atm}), absorption from the supplied gas (C_{abs}), and bacterial oxidation (C_{bac}). CO₂ fixation efficiency (η_f), representing to what extent the CO₂ supplied to the pond by the gas flow is fixed into algal biomass, is then defined as follows:

$$\eta_{fix} = \frac{C_{fix} \frac{C_{abs}}{C_{abs} + C_{inf} + C_{atm} + C_{bac}}}{C_{sup}} \quad (31)$$

where C_{sup} is the total amount of CO₂ bubbled into the pond. Note that all the quantities in Eq. (31) are in mole/day of CO₂ or inorganic carbon.

- CO₂ removal: CO₂ is partially or completely removed from the gas bubbles when they rise through the pond. On the other hand, CO₂ dissolved into the pond may be re-emitted into atmosphere at the surface of the pond, which is most likely to mix with the effluent gas flow if the re-emission occurs at the same surface area where the gas bubbles leave the pond. Consequently, collection of these escaping gas bubbles will very likely capture this part of the re-emitted CO₂, hence the effectiveness of CO₂ removal from the supplied gas is reduced. Note that CO₂ re-emitted at other parts of the pond surface, i.e. where no scrubbed gas bubbles exit, will not affect CO₂ removal. To quantify the CO₂ removal performance, the absolute amount of CO₂ removal, C_{rmv} , is calculated by

$$C_{rmv} = C_{sup} - C_{eff} + C_{emt} \frac{A_g}{A}, \quad (32)$$

where C_{eff} denotes CO₂ contained in the effluent gas flow, C_{emt} is the dissolved CO₂ re-emitted at the pond surface, A and A_g are the area of the total pond surface and the area of the pond surface where the effluent gas flow exits, respectively. The CO₂ removal efficiency is defined as

$$\eta_{rmv} = \frac{C_{rmv}}{C_{sup}} \quad (33)$$

Similar to Eq. (31), all the ‘C’ quantities in Eqs. (32) and (33) are in mole/day CO₂.

5. Results and discussion

Simulation was performed using the process modelling software gPROMS³³. In this section, simulation results revealing the detailed dynamics of the algal pond are first presented. Thereafter, the performance of the algal pond with and without additional gas supply is analysed based on the relevant simulation results.

5.1 Simulation of detailed dynamics

The model presented in Section 3 was able to predict detailed dynamics of the system. Figures 3a and 3b show exemplarily the cyclic steady state behaviour of a pond with gas supply simulated with all the conditions specified for the nominal case. Note that the quantity of BOD in this study refers only to that of the substrate in the feed and does not include the biomass of the microorganisms that grow in the pond. One can see from these plots how the important quantities change in the first CSTR (i.e. the one connecting to the influent wastewater) during a 24-hour period in response to the switch between daytime and night time. It is observed that the trend of Oxygen and pH shown in Figure 3b is similar to what was reported in [18] for algal ponds without gas supply. Stemming from the modelling of the mass transfer between supplied gas bubbles and the liquid phase, Figure 3c shows how the CO₂ concentration in the bubble phase varies with the vertical position in the pond, at two different times in a day.

Figure 3. Model-predicted behaviour of the algal pond.

5.2 Algal pond performance without additional gas supply

Simulations were performed to evaluate how influent BOD concentration, hydraulic retention time, and pond depth affect the performance of the pond.

Influent BOD concentration

Figure 4 shows that when influent BOD concentration increases from 100 g/m³ to 400g/m³, algal productivity is more than doubled, suggesting that CO₂ generated by the bacteria that oxidize organic carbon has been significantly beneficial to the growth of algae. However, algal productivity starts to decline after the influent BOD concentration goes beyond 500 g/m³; simulation analysis has shown that this is because of the shortage of nitrogen in the system caused by the fast growth of bacteria. The effluent BOD concentration increases slightly as the influent concentration increases from 100 g/m³ to a higher value, but

more than 90% reduction of BOD is always achieved. To reveal more details of this process, Figure 4 further shows the fluxes of CO_2 (except CO_2 in the influent and effluent water flow). Note particularly that CO_2 emitted to atmosphere at the pond surface is negative before the influent BOD concentration reaches 400 g/m^3 , indicating that atmospheric CO_2 is absorbed into the pond due to the CO_2 deficit caused by the fast growth of algae.

Figure 4. Effect of influent BOD concentration (without additional gas supply).

Hydraulic retention time (HRT) and pond depth

Under the nominal conditions but with HRT increasing from 5 to 10 days, the combined effect of a longer residence time and a lower concentration of substances in the pond generally leads to the decline of algal productivity and the BOD concentration of the effluent, as shown in Figure 5a. There is an exceptional increase of the algal production when the HRT changes from 5 to 6 days. Simulation revealed that, as the HRT increased, the increase of decay was initially weaker and subsequently stronger than the increase of growth, leading to the initial increase and the subsequent decline of the algal productivity.

At nominal conditions where influent BOD concentration is 300 g/m^3 , Figure 4 has previously shown that the pond is CO_2 -deficit and acquires CO_2 from atmosphere to meet the demand of algae. For a fixed pond volume, increasing the depth leads to the reduction of surface area, which in turn hampers the acquisition of atmospheric CO_2 and consequently reduces algal productivity. This trend is illustrated in Figure 5b. The decrease of effluent BOD concentration indicates that the growth of bacteria is enhanced,

which should be attributed to the better availability of nitrogen due to the reduced consumption by algae (which outweighs the effect of reduced O_2 supply from algal photosynthesis).

(a)

(b)

Figure 5. Effect of hydraulic retention time (a) and pond depth (b) (without additional gas supply).

5.3 Algal pond performance with additional gas supply

The behaviour of the pond becomes more complex when additional CO_2 -containing gas is supplied. Effect of design and operating parameters on the performance of the system is discussed below.

Effect of supplied gas flow rate and CO_2 fraction

Figure 6a shows clearly the benefit of additional gas supply to the production of algal biomass. At a flowrate of $10 \text{ m}^3/\text{hour}$, 67% and 84% increase of algal productivity are achieved by the supplied gas with 10% and 30% CO_2 , respectively. The rate of improvement is gradually reduced as the gas flowrate

increases and the maximum productivity is reached at around 30 m³/hour. The efficiencies of carbon fixation and removal, however, decrease significantly when the gas flowrate or CO₂ fraction increases, as shown in Figure 6b. This is because in any of the two cases, a large portion of the CO₂ absorbed from the supplied gas is re-emitted to the atmosphere at the pond surface, neither fixed into the algal biomass nor separated from the effluent gas flow captured at the surface of the pond.

(a)

(b)

Figure 6. Effect of supplied gas flowrate and CO₂ fraction on the performance of the algal pond.

Effect of pond bottom area for gas supply

It is shown above that dissolved CO₂ re-emitted to atmosphere leads to the reduction of CO₂ fixation and removal efficiencies. In the case of CO₂ removal, this links to collection of the scrubbed gas at the pond surface. Assuming the scrubbed gas is to be collected only at the surface directly above the bottom area where gas is inducted, simulations were run to investigate how the fraction of total bottom area used for gas supply would affect the performance of the system. When the fraction is 0.05, only the first of the 20

CSTRs was supplied with gas flow, while the first 10 CSTRs were involved when the fraction is 0.5, etc. Figure 7 shows that different gas supply areas pose minor changes to the algal productivity and BOD removal. For CO₂ removal, the best performance is achieved with a fraction around 0.25. This is a point where the absorption of CO₂ is relatively strong and at the same time the loss of dissolved CO₂ at the gas-collecting surface is relatively low. Before or beyond this point, either the CO₂ absorption is too weak (due to the low mass transfer area available) or too much re-emitted CO₂ is mixed with the scrubbed gas. In the case of CO₂ fixation, the efficiency generally improves as larger pond bottom area (and consequently larger mass transfer area) is used for supplying gas. Note that the bubble rising velocity, affecting mass transfer coefficient (cf. Eq. (23)) does vary when the area for gas supply changes. The overall performance of the system, however, was dominated by mass transfer area in these studies.

The above observations are associated with the specific type of gas sparging approach assumed in this work. If the gas flow is not introduced at the bottom of the pond, but rather through other designs such as a floating injector on top of the pond (forming a covered space for holding gas) or a deep carbonation column (or sump)¹⁷, the behaviour of the system can be quite different. In the case of a floating injector, both CO₂ fixation and removal are likely to be improved as the pond top area utilised for gas injection increases. In a case of a carbonation column, it typically tends to have a depth greater than that of the pond (hence a longer pathway for gas bubbles to conduct mass transfer) but with a rather small surface area (hence less dissolved CO₂ re-emitted from the column surface). This appears to be advantageous for CO₂ removal. However, a carbonation column with a depth of several meters can lead to a significant electricity cost for pumping the gas into the carbonator³⁴.

Figure 7. Effect of pond bottom area used for gas supply.

Influent BOD concentration

In this set of tests, a gas flow containing 10% CO₂ and supplied at 5m³/hour was considered. As shown in Figure 8, increase of the influence BOD concentration can improve algal productivity until the system becomes nitrogen limited. The efficiencies of CO₂ fixation and particularly removal are affected adversely by the increase of BOD in the feed. Figure 9 explains that this is caused by the surplus of dissolved CO₂ in the system due to the supply from bacteria that oxidize abundant BOD. Although in these simulation tests CO₂ blown into the pond was absorbed by the liquid phase rather completely in the first place, a large portion of the dissolved CO₂ was subsequently re-emitted into the atmosphere, a situation similar to the supply of gas at higher flowrates or CO₂ fractions as discussed earlier. This implies that a wastewater stream of high BOD content and a CO₂ containing gas flow would complete in supplying CO₂ to the system, making it difficult for the system to satisfactorily provide both of the two functions (i.e. wastewater treatment and CO₂ scrubbing) simultaneously.

Figure 8. Effect of influent BOD concentration (with additional gas supply)

Figure 9. CO₂ fluxes corresponding to different influent BOD concentrations (with additional gas supply).

Effect of hydraulic retention time and pond depth

As shown in Figures 10a and 10b, the effect of hydraulic retention time and pond depth on the algal productivity and BOD removal of the system has a trend similar to that of the case without additional gas supply (cf. Figure 5) and is rather moderate. Both increased HRT and pond depth help to improve the efficiencies of CO₂ fixation and removal. In the case of longer HRT, this effect should be attributed to the generally lower inorganic carbon content in the pond. On the other hand, increased pond depth overall leads to larger mass transfer area (due to the longer path of bubbles) between the supplied gas and the liquid phase, promoting CO₂ fixation and removal.

Figure 10. Effect of hydraulic retention time (a) and pond depth (b) (with additional gas supply)

6. Conclusions

A comprehensive mathematical model was constructed for studying algal ponds that make use of wastewater and possibly “waste” CO₂. A number of simulation studies were then carried out, to evaluate how the design and operating parameters of such a system affect its performance in terms of production of algal biomass, treatment of wastewater, and CO₂ fixation or removal. The main observations include:

- For an algal pond without additional gas supply, influent wastewater with high BOD concentration can significantly boost the growth of algae, however subject to the availability of other nutrients for which algae and bacteria compete, e.g. nitrogen as observed in the tested cases;

- ii) When additional CO₂-containing gas is supplied, algal productivity is generally improved. On the other hand, the efficiency of CO₂ fixation and removal drops significantly with increased gas supply and CO₂ fraction;
- iii) The efficiency of CO₂ fixation (to a lesser extent) and removal (to a greater extent) deteriorates when the feed water is richer in BOD, although this is beneficial to the growth of algae when it is not limited by other nutrients (e.g. nitrogen);
- iv) The area used for the induction of gas flow into the algal pond affects CO₂ fixation and removal differently. For the former, larger area improves the efficiency. For the latter, there exists an optimal area that leads to the highest efficiency as determined by the balance between better mass transfer and avoidance of the mixing between effluent gas bubbles and dissolved CO₂ re-emitted to the atmosphere;
- v) With a depth up to 0.4m as numerically studied in this work, a shallower pond (with a fixed volume) without gas supply works better when atmospheric CO₂ is utilised by algae. When the pond is supplied by additional gas flow, a deeper pond (within the above depth range) generally works better in all aspects; and
- vi) Changes in design and operating parameters affect the removal of BOD only moderately; in all tested cases more than 90% of BOD was removed by the pond.

It should be noted that, as the first attempt of modelling the “complete” behaviour of an algal pond supplied with wastewater and CO₂-containing gas, the mathematical model contains a number of simplifications, where future refinement is possible. Furthermore, the model parameters from the literature have been adopted in this study together with a set of fixed and simplified process conditions (e.g. temperature and daily surface light supply). As such, the current modelling framework provides a basis for developing application-specific models which should be fully calibrated with respective experimental data, coupled with relevant climatic conditions.

Acknowledgement

The author would like to thank Patricia Harvey of University of Greenwich and Paul Lucas of British Sugar for their stimulating discussions on the topic researched in this work.

References

1. Dismukes, G.C.; Carrieri, D.; Bennette, N.; Ananyev, G.M.; Posewitz, M.C. Aquatic phototrophs: efficient alternatives to land-based crops for biofuels. *Current Opinion in Biotechnology*, 2008, 19, 235–240.
2. Borowitzka, M.A. Commercial production of microalgae: ponds, tanks, tubes and fermenters. *Journal of Biotechnology*, 1999, 70, 313–321.
3. Posten, C. Design principles of photo-bioreactors for cultivation of microalgae. *Eng. Life Sci.* 1990, 9, 165–177.
4. Merchuk J. C.; Garcia-Camacho, F.; Molina-Grima, E. Photobioreactor Design and Fluid Dynamics, *Chem. Biochem. Eng. Q.* 2007, 21, 345-355.
5. Lardon, L.; Helias, A.; Sialve, B.; Steyer, J.-P.; Bernard, O. Life-Cycle Assessment of Biodiesel Production from Microalgae. *Environ. Sci. Technol.*, 2009, 43, 6475–6481.
6. Kadam, K. L. Power plant flue gas as a source of CO₂ for microalgae cultivation: economic impact of different process options. *Energy Convers. Mgm* 1997, 38, S505-S510.
7. Shilton, A. N.; Mara, D. D.; Craggs, R.; Powell, N. Solar-powered aeration and disinfection, anaerobic co-digestion, biological CO₂ scrubbing and biofuel production: the energy and carbon management opportunities of waste stabilisation ponds. *Water Science & Technology*, 2008, 58, 253-259.
8. Clarens, A. F.; Resurreccion, E. P.; White, M. A.; Colosi, L. M. Environmental Life Cycle Comparison of Algae to Other Bioenergy Feedstocks. *Environ. Sci. Technol.*, 2010, 44, 1813–1819.
9. Oswald W. J. Current status of microalgae from wastes. *Chem. Engng. Progr. Symp. Ser.* 1969, 65, 87-92.
10. Oswald, W.J. Advanced Integrated Wastewater Pond Systems," In: Supplying Water and Saving the Environment for Six Billion People, *Proceedings of the 1990 ASCE Environmental Engineering Division Conference*, eds. U.P. Singh and O.J. Helweg, American Society of Civil Engineering, 1990.

11. Green, F.B.; Bernstone, L.; Lundquist, T. J.; Muir, J.; Tresan, R. B.; and Oswald, W. J. Methane fermentation, submerged gas collection, and the fate of carbon in advanced integrated wastewater pond systems. *Wat Sci Tech.* 1995, 31, 55-65.
12. Muñoz, R.; Guieysse, B. Algal-bacterial processes for the treatment of hazardous contaminants: a review. *Water Res.* 2006, 40, 2799-815.
13. Heubeck, S.; Craggs, R. J.; Shilton, A. Influence of CO₂ scrubbing from biogas on the treatment performance of a high rate algal pond. *Wat Sci Tech.* 2007, 55, 193–200.
14. de Godos, I.; Blanco, S.; Garcia-Encina, P. A.; Becares, E.; Munoz, R. Influence of flue gas sparging on the performance of high rate algae ponds treating agro-industrial wastewaters, *Journal of Hazardous Materials*, 2010. 179, 1049-1054.
15. Park, J. B. K.; Craggs, R. J. Wastewater treatment and algal production in high rate algal pond with carbon dioxide addition. *Water Science and technology*, 2010, 61, 633 – 639.
16. Shang, H.; Scott, J. A.; Shepherd, S. H.; Ross, G. M. A dynamic thermal model for heating microalgae incubator ponds using off-gas. *Chemical Engineering Science*, 2010, 65, 4591–4597.
17. Becker, E. W. *Microalgae. Biotechnology and microbiology*. Cambridge University Press. 1994.
18. Buhr, H. O.; Millar, S. B. A dynamic-model of the high-rate algal bacterial wastewater -treatment pond. *Water Res.* 1983, 17, 29–37.
19. Jupsin, H.; Praet, E.; Vassel, J. L. Dynamic mathematical model of high rate algal ponds (HRAP). *Wat Sci. Technol.* 2003, 48, 197–204.
20. Kroon, B. M. A.; Ketelaars, H. A. M.; Fallowfield, H., J.; Mur, J. R. Modelling microalgal productivity in a High Rate Algal Pond based on wavelength dependent optical properties. *J App Phycol* 1989, 1, 247-256.
21. Fallowfield, H. J.; Mesple, F.; Martin, N. J.; Casellas, C.; Bontoux, J. Validation of computer-models for high-rate algal pond operation for waste-water treatment using data from Mediterranean and Scottish pilot scale systems-implications for management in coastal regions. *Wat. Sci. Technol.* 1992, 25, 215–224.

22. Mesple, F.; Casellas, C.; Troussellier, M.; Bontoux, J. Modelling orthophosphate evolution in a high rate algal pond. *Ecol. Model.* 1996, 89, 13–21.
23. Bordel, S.; Guieysse, B.; Munoz, A. Mechanistic Model for the Reclamation of Industrial Wastewater s Using Algal-Bacterial Photobioreactors. *Environ. Sci. Technol.* 2009, 43, 3200–3207.
24. Azov Y. Effect of pH on inorganic carbon uptake in algal cultures. *Applied and Environmental Microbiology*, 1982, 43, 1300-1306.
25. Smith, R.A. The theoretical basis for estimating phytoplankton production and specific growth rate from chlorophyll, light and temperature data. *Ecol. Model.* 1980, 10, 243–264.
26. Zhang, D.; Deen, N.G.; Kuipers, J.A.M. Numerical modeling of hydrodynamics, mass transfer and chemical reaction in bubble Columns. *6th International Conference on Multiphase Flow, ICMF 2007*, Leipzig, Germany, July 9 – 13, 2007. Paper No 265, 2007.
27. Kulkarni, A. A. Mass Transfer in Bubble Column Reactors: Effect of Bubble Size Distribution. *Ind. Eng. Chem. Res.* 2007, 46, 2205-2211.
28. Maceiras, R.; Alves, S. S.; Cancela, M. A.; Alvarez, E. Effect of bubble contamination on gas–liquid mass transfer coefficient on CO₂ absorption in amine solutions. *Chemical Engineering Journal* 2008, 137, 422–427.
29. Lívanský, K.; Doucha, J. Evaluation of dissolved oxygen (DO) profiles in microalgal suspension on outdoor thin-layer cultivation surface. *Algological Studies*, 2003, 110, 151-165.
30. Frank, M. J. W.; Kuipers, J. A. M.; van Swaaij, W. P. M. Diffusion Coefficients and Viscosities of CO₂ + H₂O, CO₂ + CH₃OH, NH₃ + H₂O, and NH₃ + CH₃OH Liquid Mixtures. *J. Chem. Eng. Data* 1996, 41, 297-302.
31. Akita, K.; Yoshida, F. Bubble Size, Interfacial Area, and Liquid-Phase Mass Transfer Coefficient in Bubble Columns. *Ind. Eng. Chem. Process Des. Develop.*, 1974, 13, 84-91.
32. Beran, B.; Kargi, F. A dynamic mathematical model for wastewater stabilization ponds. *Ecological Modelling*, 2005, 181, 39–57.
33. Process Systems Enterprise. *gPROMS Users Guide*. Process Systems Enterprise Ltd., 2010.

34. Stephenson, A. *The sustainability of first and second generation biofuels using life-cycle analysis*. PhD Dissertation, Department of Chemical Engineering and Biotechnology, University of Cambridge, 2009.
35. Steele, J. H. Environmental control of photosynthesis in the sea. *Limnology and Oceanography*, 1962, 7, 137-150.
36. Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The properties of gases and liquids*. 4th edition. McGraw Hill, 1987.