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Integration of CO₂ Absorption from Flue Gas with CO₂ Assimilation by Microalgae Using a Coupled Chemical-Biological Model

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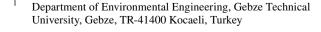
Abstract

Integration of conventional amine-based CO_2 capture systems with microalgae cultivation systems might be a promising strategy to overcome the challenges of energy requirement and the limitations in the utilization of captured CO_2 . However, integrating these two very different systems forms a more complex system. In this paper, a coupled chemical-biological model was developed to reduce the complexity of a proposed integrated system for a better understanding of the critical process parameters. The proposed system uses an aqueous tertiary alkanolamine solution to capture CO_2 from flue gases and delivers part of the captured CO_2 to microalgae after mixing the CO_2 -rich absorption solution with a nutrient solution. The model simulates the processes of CO_2 absorption-desorption and microalgae CO_2 assimilation by using chemical equilibrium principles and Monod kinetics in an integrated way and estimates biomass production rates and CO_2 utilization efficiencies for a given set of process parameters. The sensitivity analysis of the model revealed that the overall efficiency of the integrated system is primarily determined by the type of alkanolamine used in the absorption solution and the maximum alkanolamine concentration in the growth medium. The model predicted that among the four types of alkanolamine selected in this study, N-methyldiethanolamine could be a more favorable CO_2 absorbing chemical for such systems, and thus deserves to be investigated more in future studies.

Keywords CO_2 absorption · Aqueous alkanolamine solution · Microalgae · CO_2 assimilation · Monod kinetics · Modeling

Nomenclature		$C_{T, TA, GM}$	Total concentration of tertiary alkanolamine in	
A_W	Alkalinity contribution from the water (mM)	, ,-	the growth medium (mM)	
AS	Absorption solution	GM	Growth medium	
$C_{i, AS}$	Total inorganic carbon concentration in the	$[H^+]$	Concentration of hydrogen ions (mM)	
,	absorption solution (mM)	$[HCO_3^-]$	Bicarbonate concentration in the solution	
$C_{i, GM}$	Inorganic carbon concentration in the growth	2 33	(mM)	
., -	medium after reaching equilibrium with CO ₂	$[H_2CO_3^*]$	Dissolved carbon dioxide concentration in the	
	concertation in air (mM)		solution (mM)	
$C_{i, mix}$	Inorganic carbon concentration in the mixture	$K_{a1,c}$	First dissociation constant of carbonic acid (-)	
	of the absorption and nutrient solutions (mM)	$K_{a2,c}$	Second dissociation constant of carbonic acid	
$C_{i, NS}$	Total inorganic carbon concentration in the		(-)	
	nutrient source (mM)	$K_{a, TA}$	Dissociation constant of a tertiary alkanola-	
ΔC_i	The difference in inorganic carbon content		mine (-)	
	between $C_{i, mix}$ and $C_{i, GM}$ (mM)	K_{Ci}	Half saturation constant for inorganic carbon	
$[CO_3^{2-}]$	Carbonate concentration in the solution (mM)		utilization (mM)	
$C_{T, TA, AS}$	Total concentration of tertiary alkanolamine in	k_d	Decay coefficient for microalgae (day ⁻¹)	
	the absorption solution (mM)	K_{H,CO_2}	Henry's constant of carbon dioxide (-)	
		K_w	Dissociation constant of water (-)	
☐ Unal Sen		μ	Specific growth rate (day ⁻¹)	
usen@gtu.edu.tr		μ_{max}	Maximum specific growth rate (day ⁻¹)	
1		NS	Nutrient solution	

 $[OH^{-}]$





Concentration of hydroxide ions (mM)

 $P_{CO_2,f}$ Partial pressure of carbon dioxide in the flue gas (atm) Partial pressure of carbon dioxide in the air $P_{CO_2,a}$ (atm) pH_{AS} pH of the absorption solution (-) pH of the growth medium (-) pH_{GM} Acid dissociation constant of tertiary alkanola $pK_{a,TA}$ Inorganic carbon utilization rate (g L⁻¹ day⁻¹) r_{Ci} Biomass growth rate (g L⁻¹ day⁻¹) $\stackrel{r_g}{Q}_{AS}$ Flowrate of the absorption solution into the microalgae bioreactor (L s⁻¹) Q_T Flowrate of the total inflow to the microalgae bioreactor (L s⁻¹) Flowrate of the absorption solution into the Q_{NS} microalgae bioreactor (L s⁻¹) TA Tertiary alkanolamine **CUE** Carbon dioxide utilization efficiency of the integrated system (%) VVolume of the microalgae bioreactor (L) X Biomass concentration in the microalgae bioreactor (g L⁻¹) Y_{Ci} Yield coefficient for inorganic carbon utiliza-

tion (g DWB g⁻¹ C)

Introduction

Virtually all modern human activity is responsible for recent increases in carbon dioxide (CO₂) levels in the earth's atmosphere. Especially, the CO₂ emissions sourced from fossil fuel combustion for electricity and cement production are the main drivers of this increase. Each year, approximately 37 Gt of CO₂ is emitted into the atmosphere globally as a result of all anthropogenic activities and about 60% of these emissions come from fossil fuel-fired power plants, cement kilns, refineries, and other fossil fuel-based industrial sources (IPCC 2005; Le Quéré et al. 2018). CO₂ emissions from such large stationary sources, which are the largest point sources of CO₂ emissions, are managed to be reduced by three major approaches: pre-combustion capture, oxy-fuel process, and post-combustion capture (IPCC 2005). Among other approaches, post-combustion capture technologies have gained more attention due to their easier implementation to the existing combustion facilities. So far, several separation techniques such as adsorption, cryogenic separation, membrane separation, physical absorption, and chemical absorption were applied as a post-combustion technology for capturing CO₂ from flue gases generated by the point sources (IPCC 2005). Currently, the CO₂ capture technologies furthest along in development are based primarily on chemical absorption processes. Especially, the scrubbing processes using aqueous amine solutions have almost a century of use and know-how developed within the industrial applications (Bara 2012). So far, several proprietary amine mixtures were used to capture CO_2 from flue gases at different demonstration projects around the world, such as a demonstration plant using Mitsubishi Heavy Industries' KS-1® solvent in the USA (Iijima et al. 2012), a mobile test unit using Aker Solutions' S26® solvent in Norway (Knudsen et al. 2014), and a pilot plant using BASF's novel amine-based solvent, OASE® to capture CO_2 from a coal-fired power plant flue gas in USA (Krishnamurty 2016).

Amine-based CO₂ capture is a well-understood and widely-studied process which involves the reaction of CO₂ with aqueous solutions of amines in an absorption unit to form a weakly bonded intermediate compound, which is subsequently regenerated in a stripping column with the application of heat or pressure-swing. After the stripping process, the released CO₂ is collected by a condenser and compressed to 100 to 150 bar for industrial use or geologic sequestration (Rochelle 2009). While amine-based processes are capable of capturing more than 90% of CO₂ from flue gas streams, there are still some issues to be resolved before wide industrial applications, such as high energy consumption in the amine regeneration step, and the limitations in the use of high-purity CO₂ captured during the absorption process (Rochelle 2009; Bara 2012). Amine regeneration step requires a large amount of energy input, constituting up to 70% of the total operating cost of a typical CO₂ capture plant. Thus, the installation of an amine-based CO₂ capture plant to an existing power plant is estimated to increase the use of electricity by about 75-80% (Idem et al. 2006; NETL 2013). In addition to high energy penalties of the desorption process, only a small portion of the CO₂ captured from flue gas emissions can be utilized as a chemical feedstock in the industry due to limited use of CO₂ in manufacturing of chemicals (Bara 2012). For handling captured CO₂, geological sequestration is also considered as a promising option for 2 due to extremely large storage capacities of existing saline aguifers. On the other hand, there are still several uncertainties and risks associated with long-term CO₂ storage in providing assurance of limited leakage rates and longterm liability for maintenance and monitoring of stored CO₂ (Anderson 2016).

An alternative to the current approach, i.e. amine-based CO_2 capture followed by geological sequestration of captured CO_2 , is to use fast growing photosynthetic organisms (microalgae, cyanobacteria, etc.) to assimilate CO_2 emissions from flue gases. Assimilation of CO_2 by microalgae is based on utilizing flue gas CO_2 as an inorganic carbon source for photosynthesis to produce algal biomass. Compared to the current approach, capturing and assimilation of CO_2 by microalgae has some benefits, including low energy and chemical requirements, and production of commercially viable biomass. However, there are some challenges to be



addressed before the full implementation of this technology. The most challenging task is to deliver gaseous CO₂ efficiently to the algal ponds. Typical algal ponds are designed to maximize light penetration by having shallow depths and high area-to-volume ratios compared to conventional bioreactors (Apel and Weuster-Botz 2015). When CO₂-rich flue gas is bubbled into such algal ponds, CO₂ escape to the atmosphere becomes high, and CO₂ utilization efficiency remains low between 10 and 30% of the supplied amount (Li et al. 2013). Creating microbubbles by fine diffusers (Zimmerman et al. 2009), directly solubilizing CO_2 into the medium by passing through dense membranes (Kim et al. 2011) or intermittent CO₂ delivery were proposed to increase CO₂ transfer efficiency to algal ponds (Li et al. 2013). Although these methods caused substantial increases in CO₂ transfer efficiencies in lab-scale experiments, possible diffuser clogging problems and increased energy penalties due to pressurized CO₂ delivery brings into question the real-scale implementation of these methods (Zheng et al. 2017). In addition to this, it is difficult to find places having sufficient and low-cost sources of both CO₂ and nutrient solution (wastewater, etc.) in the vicinity of each other. Thus, compression and transportation of CO₂ from the CO₂ point source to the algal ponds will be needed (Benemann and Oswald 1996). Yet, high operational costs make this alternative totally impractical. It must also be taken into account the additional costs for storage of captured CO₂ during the night or winter periods when algae have no or low photosynthetic activity (Chi et al. 2011).

A promising strategy to overcome the limitations arising from the use of gaseous CO₂ in microalgae CO₂ assimilation process is to convert gaseous CO₂ into bicarbonate/carbonate forms in aqueous solutions using conventional absorption processes and, then to supply inorganic carbon to algal cultures in dissolved bicarbonate form. It is obvious that supplying inorganic carbon as aqueous bicarbonate solution not only could diminish the CO2 loss encountered with the use of gaseous CO₂, but also could reduce CO₂ transportation and storage costs drastically. It is already known that both microalgae and cyanobacteria are capable of uptake of bicarbonate ions through their membranes and use them as their carbon source after converting them to CO₂ using a special enzyme called carbonic anhydrase (Raven et al. 2008). Various microalgae and cyanobacteria species could reach significant biomass production rates when bicarbonate salts (mostly sodium bicarbonate (NaHCO₃)) are used as a sole carbon source instead of gaseous CO₂ supply (White et al. 2012; Chi et al. 2014; Kishi and Toda 2018). In addition, it was reported that different types of aqueous amine solutions could serve to deliver bicarbonate ions to microalgae up to certain amine concentrations without affecting biomass growth rates (Choi et al. 2012; Kim et al. 2013; Sun et al. 2015; Sun et al. 2016).

In these studies, aqueous amine solutions were added to microalgae growth mediums to capture some of the gaseous CO₂ supplied for microalgae cultivation in order to lower the CO₂ loss. However, it would be more practical and costeffective if aqueous amine solutions are first loaded with flue gas CO₂ in gas absorbers, then transported to microalgae cultivation facilities, and mixed with growth medium before the cultivation step, and then recovered by a separation technique at the exit of the ponds and finally reused in the absorber as CO₂ capturing solvent again. However, the integration of these two very different processes (CO₂) absorption and CO₂ assimilation by microalgae) creates a more complex system including several critical parameters (pH, alkalinity, etc.) and constraints (toxicity of absorbents, etc.) (Song et al. 2019). Thus, economically and technically feasible conversion of captured CO₂ to microalgae biomass would require a better understanding of the major process parameters of such an integrated system and their effects on system outputs.

In this paper, a coupled chemical-biological model is proposed, for the first time, to predict the major parameters and the critical constraints to be considered to be able to successfully integrate the amine-based flue gas CO₂ absorption process and the process of CO₂ assimilation by microalgae. The model is a coupled chemical-biological model that is composed of two parts: (1) CO₂ absorption-desorption part which is based on aqueous carbonate equilibrium to calculate the amount of CO2 absorbed by an amine solution from typical flue gas and the amount of CO₂ desorbed when the CO₂ loaded absorption solution is mixed with a nutrient solution and (2) CO₂ assimilation part which is based on Monod growth kinetics to estimate subsequent growth rate after assimilation of CO₂ released from the mixture. Thus, the main objectives of this study are to identify major process parameters and constraints of the integrated system, to determine how sensitive the proposed model is to selected system parameters, and to estimate CO2 assimilation rate and CO₂ utilization efficiency of the integrated system for a given set of parameters and constraints.

Methods

Description of the Proposed Integrated System

A schematic design of the proposed conceptual integrated system is given in Fig. 1. The system mainly consists of two separate facilities which could be located close to or far away from each other. The first facility includes a stationary point source of CO₂ (e.g., a power plant or a cement kiln) and a nearby CO₂ absorption tower that uses an aqueous amine solution as an absorption solution (AS) to capture CO₂ from the flue gas. The second



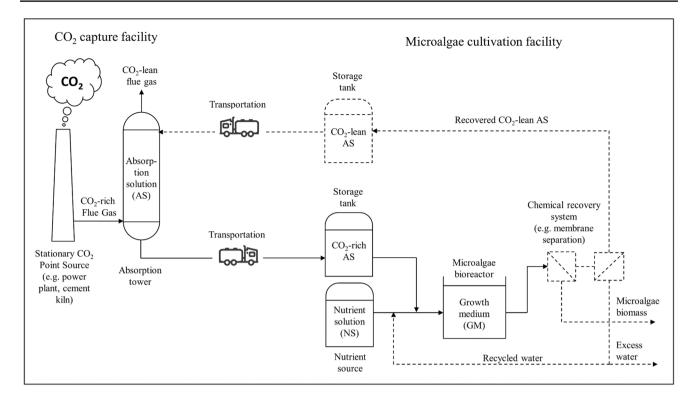


Fig. 1 Schematic design of the proposed conceptual integrated system

one is a microalgae cultivation facility that has an open microalgae bioreactor. This facility is located close to a nutrient source (e.g., wastewater treatment plant), which discharges an effluent stream containing necessary nutrients for microalgae growth and is defined here as the nutrient solution (NS). This microalgae cultivation facility also includes a harvesting unit for biomass recovery and chemical recovery and storage units for handling and recovery of amine from the effluent of the microalgae bioreactor. In the first facility, CO₂ in flue gas is captured in CO₂ lean AS; the resulting CO₂-rich solution is then transferred to the second facility by a cost-effective transportation system (trucks, pipeline, etc.). The solution is first stored in a closed vessel and then delivered to the bioreactor after mixing with the nutrient medium at certain mixing ratios. The CO₂-rich solution is expected to release some part of its CO₂ content into the growth medium (GM) where microalgae could assimilate the CO₂ released during their photosynthesis. After the cultivation step, microalgae biomass is harvested in a separate harvesting unit. The CO₂ absorbing amine compounds remaining in the effluent of the harvesting unit are removed and concentrated by a separation system (e.g., membrane filtration). The concentrated amine is stored within the facility and, then transferred to the gas absorption facility to be reused in the CO₂ capture process.

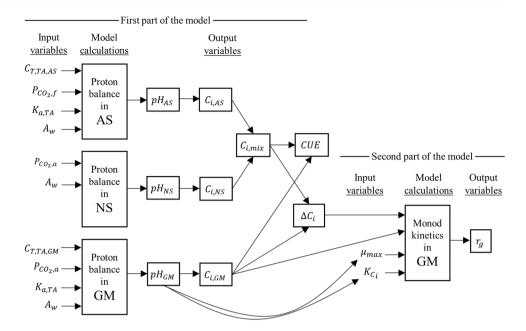
Description of the Model

The goal of the integrated system is to provide a viable alternative for the utilization of CO₂ captured from the flue gas by maximizing CO₂ assimilation by microalgae. Therefore, the main purpose of the model is to estimate the potential outputs of the proposed integrated system in terms of biomass production and carbon dioxide utilization efficiency for a given set of input variables. These outputs are mainly controlled by two main processes: (1) CO₂ absorption-desorption process and (2) microalgal CO₂ assimilation process. Thus, the model only focuses on CO₂ absorption-desorption and microalgae CO₂ assimilation steps in the integrated system and leaves the biomass harvesting and chemical recovery steps out of the scope of this paper.

As depicted in Fig. 2, the model consists of two parts. In the first part, the model uses the main process parameters $(C_{T, TA, AS}, P_{CO_2,f}, K_{a, TA}, A_w)$, and $C_{T, TA, GM}$ as input variables to obtain total inorganic carbon contents of the absorption and nutrient solutions, and the growth medium $(C_{i, AS}, C_{i, NS} \text{ and } C_{i, GM})$, respectively. These total inorganic carbon concentrations are then used in the model to calculate the mixture of the absorption and the nutrient solutions $(C_{i, mix})$, the amount of inorganic carbon released into the growth medium (ΔC_i) and the carbon dioxide utilization efficiency (CUE) of the system. The second part of the model estimates



Fig. 2 Description of the model structure



the daily biomass growth rate of a specific microalgae species by using concentration differences in inorganic carbon content (ΔC_i) calculated in the first part and pH-dependent growth kinetic constants (μ_{max} and K_{C_i}). Here, it is assumed that all of the inorganic carbon content released into the growth medium is assimilated by microalgae. More detail about the model equations and parameters is given in the following parts.

Absorption and Desorption of CO₂

The first part of the model focuses on chemical equilibrium reactions in a typical gas absorption-desorption process using an alkanolamine solution for capturing CO₂ from a flue gas stream. Alkanolamine solutions, which have long been used to remove CO₂ from flue gases, are aqueous solutions of chemical compounds that contain both hydroxyl and amino functional groups on an alkane backbone. They are classified into primary, secondary, and tertiary alkanolamines based on the number of the attached amine group. CO₂ capture by amines can be described by two different mechanisms: (1) for primary and secondary alkanolamines, the mechanism involves carbamate formation through reactions with CO₂ (Caplow 1968), (2) for tertiary alkanolamines, the amine group acts as a base catalyst, increases the reactivity of water towards CO₂ and consequently forms bicarbonate ions by reacting with CO₂ (Donaldson and Nguyen 1980). The primary and secondary alkanolamines are widely used in CO₂ capture facilities because of their rapid reaction rates, while the tertiary alkanolamines can be used mostly in amine blends to lower the regeneration costs (López et al. 2014). In this study, aqueous tertiary alkanolamine (TA) solutions were selected as model absorption solutions because they are expected to result in less pH changes after addition to the growth medium compared to primary and secondary alkanolamines due to their higher number of hydroxyl groups (Rayer et al. 2014). Additionally, tertiary alkanolamines show less toxic effect on microalgae compared to primary and secondary alkanolamines, which create toxic carbamate intermediates during reactions with CO_2 (Kim et al. 2013).

The model was formulated first to predict the theoretical CO_2 capture capacity of a TA solution in equilibrium with a typical flue gas stream at ambient temperature (25 °C) and atmospheric pressure (1 atm). After CO_2 -rich TA solution and the nutrient solution are mixed with each other, a second equilibrium state will be reached. Since the partial pressure of CO_2 in these two equilibrium states will be different, some amount of captured CO_2 will be released into the growth medium (ΔC_i) where microalgae will be able to use for biomass production.

These equilibrium states are formulated in the model based on proton balance equations constructed in three different aqueous solutions used in the process: (1) the absorption solution in the absorption tower, (2) the nutrient solution used for microalgae cultivation, and (3) the growth medium obtained after mixing these two solutions. The proton balance is a kind of mass balance that is used to determine the final equilibrium state of a mixture of two or more solutions from the initial states of the solutions, by accounting for the variations in the proton condition of all components in acid-base reactions with respect to the change in the alkalinity (total base) of the system (Mott 2013; Nguyen and Rittmann 2015). For each solution, a separate proton balance equation was built by specifying reference species for each acid/base system: water (H₂O) for the hydronium—water—hydroxide system, carbonic acid (H₂CO₃)



for carbonate system and non-protonated amine species (R_3N) for amine buffer system. These equations are used to find the final total inorganic carbon concentration (C_i) and final pH of the solution in equilibrium with the CO_2 concentration in the flue gas or in the atmosphere.

In the absorption tower, CO₂ is absorbed into the TA solution by means of several chemical reactions taking place between CO₂, water, and TA compound. The first reaction is the dissolution of CO₂ from flue gas governed by equilibrium based on Henry's Law (Eq. (1)) and gas-liquid masstransfer kinetics. Since dissolved CO2 is present in water as hydrated CO_2 ($CO_{2(aa)}$) and carbonic acid (H_2CO_3) in specific proportions, a hypothetical species $(H_2CO_3^*)$ is used to represent the total dissolved CO_2 in the system (Eq. (2)). The dissolved CO₂ in water dissociates into other carbonate species to produce a carbonate system in equilibrium with the partial pressure of the flue gas CO₂ according to Henry's constant (K_{H,CO_2}) and two acid-dissociation constants $(K_{a1,c})$ and $K_{a2,c}$ (Eq. (3) and (4)), all specific to the system. The concentrations of inorganic carbon species vary with pH and their sum gives total inorganic carbon concentration (C_i) of the system (Eq. (5)). At the same time, dissociation of water takes place to attain an equilibrium state according to the water dissociation constant (K_w) (Eq. (6)).

$$\left[H_2CO_3^*\right] = \left[H_2CO_3\right] + \left[CO_{2(aq)}\right] \tag{2}$$

$$H_2CO_3^* \overset{K_{al,c}}{\leftrightarrow} HCO_3^- + H^+ ; K_{al,c} = 10^{-6.35} \text{ (at } 25^{\circ}\text{C)}$$
 (3)

$$HCO_3^{-} \stackrel{K_{a2,c}}{\leftrightarrow} CO_3^{-} + H^+$$
; $K_{a2,c} = 10^{-10.33}$ (at 25°C) (4)

$$C_i = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$
 (5)

$$H_2O \stackrel{K_w}{\leftrightarrow} OH^- + H^+; K_w = 10^{-14} \text{ (at } 25^{\circ}\text{C)}$$
 (6)

In aqueous absorption solution, total tertiary alkanolamine content ($C_{T,TA,AS}$) exists in both protonated (R_3NH^+) and non-protonated (R_3N) forms according to the acid dissociation constant of the corresponding TA ($K_{a,TA}$) (Eq. (7) and (8)). When, CO₂ dissolves into the solution, non-protonated TA reacts with dissolved CO₂ ($H_2CO_3^*$) and forms an unstable complex consisting of protonated TA and bicarbonate ion Eq. (9).

$$R_3NH^+ \stackrel{K_{a,TEA}}{\leftrightarrow} H^+ + R_3N \tag{7}$$



$$R_3N + H_2CO_3^* \leftrightarrow R_3NH^+ + HCO_3^-$$
 (9)

Considering the reactions (Eq. (1)–(7)) and the reference species given above, the proton balance in the absorption solution can be described as:

$$[R_3NH^+] + [A_w] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$
(10)

Water used in the absorption solution will have some amount of alkalinity contribution which is considered in the proton balance by adding a term (A_w) to the left side of the equation. The equation can be rewritten by substituting the individual concentrations of species by their fractional expressions as a function of $[H^+]$ (Eq. (11)).

$$C_{T,TA,AS} \frac{[H^{+}]}{[H^{+}] + K_{a,TA}} + [A_{w}] = \frac{\frac{P_{CO_{2}f}}{K_{H,CO_{2}}} K_{a1,c}}{[H^{+}]} + 2 \frac{\frac{P_{CO_{2}f}}{K_{H,CO_{2}}} K_{a1,c} K_{a2,c}}{[H^{+}]^{2}} + \frac{K_{w}}{[H^{+}]} - [H^{+}]$$
(11)

This new form of the equation indicates that for a given set of input parameters $(Alk_w, C_{T, TA, AS}, K_{a, TA}, \text{ and } P_{CO_2f})$ and equilibrium constants $(K_H, K_{a1, c}, K_{a2, c}, \text{ and } K_w)$, only one equilibrium hydrogen ion ([H⁺]) concentration (or pH) will satisfy Eq. (11).

A generalized reduced gradient non-linear optimization algorithm (Microsoft Excel Solver; Microsoft) was used to obtain this single value of $[H^+]$ concentration (or pH) at the equilibrium state by minimizing the difference between both sides of the proton balance equation with several iterations. That $[H^+]$ value was then used to find the total inorganic carbon concentration (C_i) of the absorption solution by using Eq. (5) after re-writing it as a function of $[H^+]$ in Eq. (12).

$$C_{i} = \frac{P_{CO_{2},f}}{K_{H}} + \frac{\frac{P_{CO_{2},f}}{K_{H,CO_{2}}}K_{a1,c}}{[H^{+}]} + \frac{\frac{P_{CO_{2},f}}{K_{H,CO_{2}}}K_{a1,c}K_{a2,c}}{[H^{+}]^{2}}$$
(12)

The same procedure was also applied for the nutrient solution to find equilibrium pH value and total inorganic carbon concentration. Different from the absorption solution, the nutrient solution doesn't include TA species in its proton balance and the nutrient medium was assumed to be in equilibrium with global atmospheric CO_2 concentration $(P_{CO_2,a})$ which was recorded in 2019 with an annual average CO_2 concentration of 410 ppm (Dlugokencky and Tans 2020). For the sake of simplicity, it was also assumed that the content of the nutrient solution is similar to a widely used nutrient medium for microalgae cultivation, i.e., BG11 medium, and the nutrient solution has the same amount of alkalinity contribution (Alk_w) from its natural water content as in the case of the absorption solution. It is plausible that



an extra alkalinity contribution will be provided by phosphate buffer system created in the nutrient solution due to its phosphate content. However, typical phosphate concentrations in standard BG11 medium (about 0.2 mM) is negligible compared to total alkalinity of a typical surface water (0.4–4 mM) (Berthouex Mac and Brown 2018). Moreover, since BG11 medium contains nitrogen in the form of nitrate (NO₃-) rather than ammonium (NH₄+), the nitrogen content of the nutrient solution has no significant effect on the alkalinity of the solution. Thus, the proton balance for the nutrient solution was constructed as depicted in Eq. (13), which includes alkalinity contribution from the natural water and neglects alkalinity contribution from the phosphate and nitrogen contents.

$$[Alk_w] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$
 (13)

Equation (13) can be expressed as a function of $[H^+]$ as:

$$\left[Alk_{w}\right] = \frac{\frac{P_{CO_{2},a}}{K_{H,CO_{2}}}K_{al,c}}{\left[H^{+}\right]} + 2\frac{\frac{P_{CO_{2},a}}{K_{H,CO_{2}}}K_{al,c}K_{a2,c}}{\left[H^{+}\right]^{2}} + \frac{K_{w}}{\left[H^{+}\right]} - \left[H^{+}\right]$$

After determining the equilibrium states of both the absorption solution and the nutrient solution, they were assumed to be mixed inside the microalgae bioreactor at different mixing ratios. As a result of mixing, the total TA concentration in the absorption solution ($C_{T,TA,AS}$) will be diluted to a new TA concentration in the growth medium $(C_{T, TA, GM})$ and the mixture will eventually reach a new equilibrium state with atmospheric CO_2 concentration ($P_{CO_2,a}$). The total TA concentration in the growth medium $(C_{T, TA, GM})$ could be regarded as a critical concentration beyond which growth rates of microalgae start to decrease due to the toxicity of TA in the medium. Since the toxicity level of TA compound is specific to the type of microalgae species, the mixing ratio of absorption solution and nutrient solution is constrained by the maximum concentration of TA to be tolerated in the growth medium $(C_{T,TA,GM})$. Thus, the proton balance in the growth medium can be constructed as in Eq. (15) as a function of $[H^+]$ by using $C_{T, TA, GM}$ as the equilibrium concentration of TA after mixing.

$$C_{T,TA,GM} \frac{\left[H^{+}\right]}{\left[H^{+}\right] + K_{a,TA}} + \left[A_{w}\right] = \frac{\frac{P_{CO_{2},a}}{n_{CO_{2}}} K_{a1,c}}{\left[H^{+}\right]} + 2 \frac{\frac{P_{CO_{2},a}}{K_{n_{LO_{2}}}} K_{a1,c} K_{a2,c}}{\left[H^{+}\right]^{2}} + \frac{K_{w}}{\left[H^{+}\right]} - \left[H^{+}\right]$$
(15)

Mass balance for inorganic carbon after mixing the absorption solution (AS) with the nutrient solution (NS) can be simply depicted as:

$$C_{i,mix} = \frac{Q_{AS}C_{i,AS} + Q_{NS}C_{i,NS}}{Q_{T}}$$
 (16)

 Q_{AS} and Q_{NS} are the flowrates of the absorption solution and the nutrient solution, respectively. After mixing

together, these two flowrates are summed up to produce the total inflow to the growth reactor (Q_T) . $C_{i,\ mix}$ is the inorganic carbon concentration in the mixture that serves as the influent on the algae growth reactor. In the growth reactor a large part of $C_{i,\ mix}$ will be used for algae growth, leaving a relatively low inorganic carbon concentration in the growth medium that will be determined, according to the Henry's Law, by the atmospheric CO_2 concentration $(P_{CO_2,a})$. At equilibrium, the inorganic carbon concentration in the growth medium is depicted here by $C_{i,\ GM}$. It should be noted that any escape of CO_2 from the growth medium to the atmosphere is considered negligible in the model. Thus, inorganic carbon concentration which will be available for the growth of algae, (ΔC_i) , can simply be represented as

$$\Delta C_{i} = C_{i,mix} - C_{i,GM} \tag{17}$$

In the model, it was assumed that ΔC_i is captured completely by microalgae in the growth medium and assimilated to produce biomass. In other words, in our model calculations, the rate of CO_2 released during mixing was taken to be equal to CO_2 uptake rate of microalgae. In addition to that, the carbon dioxide utilization efficiency (CUE) of the integrated system was calculated to reveal the relative performance of the proposed integrated system compared to other CO_2 utilization processes. The (CUE) of the system can be defined and estimated by:

CUE =
$$100 \times \left(\frac{C_{i,mix} - C_{i,GM}}{C_{i,mix}}\right) = 100 \times \left(\frac{\Delta C_i}{C_{i,mix}}\right)$$
 (18)

CUE of the integrated system shows in percentile how effectively the CO₂ absorbed in the absorption tower could be utilized by microalgae for selected system conditions.

Assimilation of CO₂ by Microalgae

The second part of the model uses the calculated inorganic carbon available for the growth of microalgae in the first part of the model (ΔC_i) as an input to predict biomass growth rate and CUE during the assimilation of CO_2 by microalgae. The growth model assumes that ΔC_i acts as the limiting nutrient that controls the growth rate of microalgae, while other nutrients (nitrogen, phosphorus, and micronutrients) are present in excess amounts. The growth kinetics was described by the most widely used and successfully applied growth kinetics relationship, the Monod equation (Eq. (19)):

$$\mu = \frac{\mu_{max} C_i}{K_{Ci} + C_i} \tag{19}$$

where μ is the specific growth rate of microalgae, μ_{max} is the maximum specific growth rate of microalgae, C_i is the



inorganic carbon concentration in the bioreactor and K_{Ci} is the half-saturation constant which corresponds to the required inorganic carbon concentration to reach the half of the maximum specific growth rate. If it is assumed that completely, or nearly completely, mixed conditions prevail in the growth medium and the cultivation system is operated in continuous flow mode, the material balances for inorganic carbon (as the limiting nutrient) and cellular biomass concentrations can be written as follows:

$$\frac{dC_{i,GM}}{dt} = Q_{T}C_{i,mix} - Q_{T}C_{i,GM} - r_{Ci}V$$
 (20)

$$V\frac{dX}{dt} = Q_T X_0 - Q_T X + \mu XV - k_d XV$$
 (21)

where r_{Ci} is inorganic carbon utilization rate of microalgae, V is the volume of the growth medium, X_0 is incoming microalgae biomass concentration to the growth medium, X is the microalgae biomass concentration in the growth medium and k_d is the decay coefficient for microalgae. Under steady state conditions, the inorganic carbon and biomass concentrations in the growth medium do not change with time. Under these conditions, Eq. (20) and (21) can be equated to zero. Also, X_0 and k_d can be set equal to zero assuming that there is no incoming microalgae biomass in the inflow to the system, and the decay rate of the microalgae grown in the growth medium will be negligible under a high rate of growth. Eq. (20) and (21) can then be rewritten as follows, respectively:

$$r_{Ci} = \frac{Q_T C_{i,mix} - Q_T C_{i,GM}}{V} \tag{22}$$

$$\mu = \frac{Q_T}{V} \tag{23}$$

Since it was assumed that microalgae growth was assumed to be limited only by the inorganic carbon content available to microalgae, the inorganic carbon utilization rate is directly proportional to the microalgae biomass production rate as in Eq. (24).

$$r_{Ci} = \frac{r_g}{Y_{Ci}} \tag{24}$$

where r_g is the biomass growth rate and Y_{Ci} is the inorganic carbon yield coefficient, which represents the unit increase in dry weight biomass (DWB) produced per unit amount of inorganic carbon utilized. Finally, the biomass growth rate can be calculated by substituting Eq. (16), (19), (23), and (24) into Eq. (25) as follows:



As can be seen from Eq. (25), biomass production is a function of several parameters. $C_{i GM}$ and ΔC_{i} are primarily determined by the equilibrium states reached during the absorption of CO₂ into CO₂-lean absorption solution in the absorption tower and the desorption process during injection of the CO₂-rich absorption solution to the microalgae bioreactor. On the other hand, Y_{Ci} , μ_{max} , and K_{Ci} depend on the characteristics of microalgae species, which should be determined analytically and experimentally for each species. In many of the earlier studies (Goldman et al. 1974; Goldman and Graham 1981; Clark et al. 1999; Clark and Flynn 2000; Nguyen and Rittmann 2016), these parameters were determined for microalgae under carbon limited growth conditions. As can be seen in Table 1, μ_{max} and K_{Ci} change from species to species as well as for a single species with the change of the medium pH, while Y_{Ci} stays nearly constant for all species at about 2 g DWB g⁻¹ C, which corresponds to a typical carbon content (50%) of microalgae cells (Chisti 2007). In one of these studies, the inorganic carbon yield coefficient (Y_{Ci}) of microalgae was shown to be independent of growth rate and initial inorganic carbon concentration (Goldman and Graham 1981). Thus, in our study, the yield coefficient (Y_{C_i}) was selected as 2 g DWB g⁻¹ C for all model calculations. On the other hand, μ_{max} and K_{Ci} ranges from 0.48 to 2.49 day⁻¹ and from 12 to 720 μM, respectively, and no correlation between these two parameters could be found yet (Clark and Flynn 2000). Most K_{Ci} values of microalgae are relatively small compared to typical inorganic carbon concentration in natural waters (0.4–4 mM), which indicates that most microalgae have high affinity to inorganic carbon, and therefore any change in K_{Ci} has limited influence on the final growth rate. Besides that, μ_{max} has relatively significant effect on growth rates and varies with pH even for the same microalgae species. The pH of the growth medium controls the speciation of inorganic carbon content of the medium as well as the growth kinetics of microalgae because microalgae have different affinities to different inorganic carbon species (Goldman and Graham 1981). Thus, it can be proposed that the addition of tertiary alkanolamine to the growth medium to supply CO₂ for microalgae growth not only determines the pH of the growth medium, but also indirectly controls the growth kinetics of microalgae by changing the speciation of inorganic carbon content of the medium. Since, our model estimates the pH of the growth medium after reaching the equilibrium, the pH dependent values of the growth parameters (μ_{max} and K_{Ci}) can be estimated by using pH values obtained from the first part of the integrated model. For model predictions, the growth parameters found by Nguyen and Rittmann (2016)



Table 1 Comparison of inorganic carbon limited growth parameters

Species	μ_{max} (day ⁻¹)	K_{Ci} (μ M)	<i>Y_{Ci}</i> (g DWB g ⁻¹ C)	Study
Scenedesmus quadricauda	2.08 (pH = 7.1) 2.30 (pH = 7.3) 2.15 (pH = 7.5)	12 (pH = 7.1) 30 (pH = 7.3) 45 (pH = 7.5)	2.24	Goldman and Graham (1981)
Scenedesmus capricornutum	2.43 (pH = 7.1) 2.29 (pH = 7.3) 2.49 (pH = 7.5)	34 (pH = 7.1) 53 (pH = 7.3) 124 (pH = 7.5)	2.05	
Chlorella vulgaris	$2.11 \pm 0.04 (pH = 7.2)$	$17 \pm 2 \text{ (pH} = 7.2)$	2.17 ± 0.34	Goldman and Graham (1981)
Scenedesmus obliquus	$1.59 \pm 0.03 \text{ (pH} = 7.2)$	$13 \pm 4 \text{ (pH} = 7.2)$	2.08 ± 0.36	
Isochrysis galbana	$0.48 \pm 0.01 \text{ (pH} = 8.3)$	$81 \pm 1 \text{ (pH} = 8.3)$		Clark et al. (1999)
Phaeodactylum tricornutum	$0.79 \pm 0.07 (\text{pH} = 8.3)$	$30 \pm 2 \text{ (pH} = 8.3)$		
Thalassiosira pseudonana	$1.33 \pm 0.11 \text{ (pH} = 8.3)$	$273 \pm 7 \text{ (pH} = 8.3)$		Clark and Flynn (2000)
Thalassiosira weissflogii	$1.55 \pm 0.08 (\text{pH} = 8.3)$	$258 \pm 4 \text{ (pH} = 8.3)$		
Stichococcus bacillaris	$0.77 \pm 0.08 (\text{pH} = 8.3)$	$720 \pm 2 \text{ (pH} = 8.3)$		
Emiliania huxleyi	$1.19 \pm 0.10 (pH = 8.3)$	$150 \pm 5 \text{ (pH} = 8.3)$		
Heterosigma carterae	$1.21 \pm 0.10 (pH = 8.3)$	$673 \pm 1 \text{ (pH} = 8.3)$		
Synechocystis sp. PCC 6803	$2.03 \pm 0.05 \text{ (pH} = 7.5)$ $2.37 \pm 0.04 \text{ (pH} = 8.5)$ $2.00 \pm 0.07 \text{ (pH} = 9.5)$	$86 \pm 12 \text{ (pH} = 7.5)$ $85 \pm 7 \text{ (pH} = 8.5)$ $96 \pm 17 \text{ (pH} = 9.5)$		Nguyen and Rittmann (2016)

for *Synechocystis* sp. PCC 6803 (in Table 1) were selected due to their availability for quite a wide range of pH values (7.5–9.5) under CO₂ limited conditions. The measured values of the growth parameters were interpolated linearly between two adjacent pH values (7.5–8.5 and 8.5–9.5) to find the corresponding values of the growth parameters for each equilibrium pH calculated for different TA concentrations in the growth medium. As a result, the model predicts the daily biomass growth rates of the selected microalgae species for different equilibrium pH values attained by mixing absorption solution and nutrient solution at different mixing ratios.

Sensitivity Analysis

A sensitivity analysis of the proposed model was conducted in order to identify the contributions of individual process parameters ($C_{T, TA, AS}$, $P_{CO_2,f}$, $K_{a, TA}$, A_w , and $C_{T, TA, GM}$) on critical intermediate output variables (pH_{AS} , $C_{i, AS}$, pH_{GM} , $C_{i, mix}$, $C_{i, GM}$, and ΔC_i) and final model outputs (r_g and CUE). The sensitivity of the model to the selected variables was determined by changing one input variable within a range of values at a time while fixing the others at their selected base values (Table 2). These base values were chosen in accordance with typical operating parameters used in conventional amine-based CO_2 systems and were regarded as baseline conditions in the sensitivity analysis.

Results and Discussion

Sensitivity of the Model to Process Parameters

Figures 3 and 4 are constructed for the absorption solution and the growth medium, respectively by simultaneously solving the model equations (Eq. 11, 12, 14, 15, 16, 17, 18, and 25) to test the sensitivity of the model to each parameter by varying each parameter over a range of values while the other parameters are held constant at the selected base values.

In the absorption solution, for a TA with a p $K_{a, TA}$ of 8.54 (MDEA), $P_{CO_2,f}$ of 0.15 atm, and A_w of 2 mM, the effect of concentration of TA ($C_{T, TA, AS}$) in the solution is presented in Fig. 3a. As would be expected, using more TA in the solution increases the amount of CO_2 captured from the flue gas, presented as $C_{i, AS}$ in the graph. However, inorganic carbon capture capacity ($C_{i, AS}/C_{T, TA, AS}$), i.e., the amount of CO_2 captured in the absorption solution per unit amount of TA, decreases with increasing $C_{T, TA, AS}$. This is because at higher

Table 2 Selected ranges and base values of the parameters in the sensitivity analysis

Process parameter	Unit	Range of values	Base value
$C_{T, TA, AS}$	M	0.25-4.75	2.5
$P_{CO_2,f}$	atm	0.03-0.3	0.15
$pK_{a, TA}^{a}$		6.6-10.5	8.5
A_w	mM	0.4-4	0.2
$C_{T, TA, GM}$	mM	5–45	25



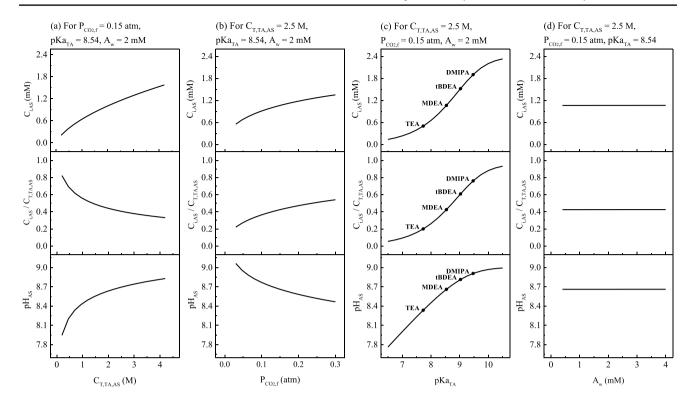


Fig. 3 Sensitivity of inorganic carbon concentration $(C_{i,AS})$, inorganic carbon capture capacity $(C_{i,AS}/C_{T,TA,AS})$, and pH (pH_{AS}) in the absorption solution to the variations in each critical system parameter: **a** $C_{T,TA,AS}$, **b** $P_{CO,f}$, **c** $pK_{a,TA}$, (d) A_w

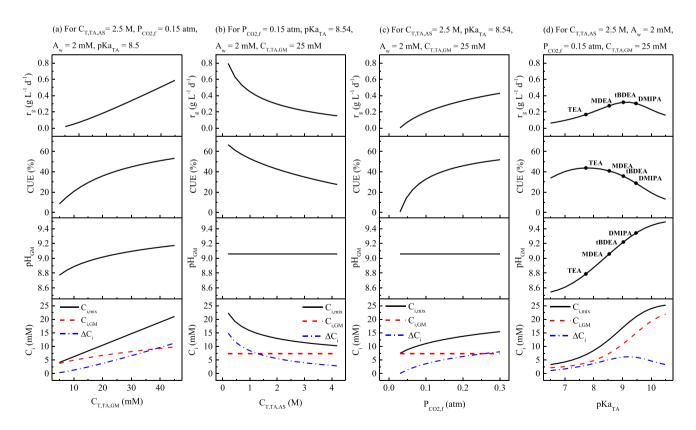


Fig. 4 Sensitivity of microalgae growth rate (r_g) , CO_2 utilization efficiency (CUE), pH in the growth medium (pH_{GM}) , and inorganic carbon concentrations $(C_{i, mix}, C_{i, GM}, \Delta C_i)$ to the variations in each critical system parameter: $\mathbf{a} C_{T, TA, GM}$, $\mathbf{b} C_{T, TA, AS}$, $\mathbf{c} P_{CO_2}$, $\mathbf{d} pK_{a, TA}$



 $C_{T, TA, AS}$ concentrations, the pH of the solution increases causing a shift in equilibrium toward non-protonated TA species, which are not effective in capturing CO_2 .

For a constant $C_{T, TA, AS}$ value (2.5 M), increasing CO_2 content in flue gas ($P_{CO_2,f}$) causes an increase in both $C_{i, AS}$ and ($C_{i, AS}/C_{T, TA, AS}$), because of the acidification of the absorption solution (Fig. 3b).

As presented in Fig. 3c, changing the $pK_{a,TA}$ value, which is equivalent to changing of the type of TA compound (all other conditions remaining the same) causes a very significant effect on all the model outputs. For the sake of comparison in the model, four different TA compounds (previously used as CO_2 capture chemicals in other studies), were selected according to their pK_a values (Table 3) and were represented with separate data points in Fig. 3c. Both $C_{i,AS}$ and $C_{i,AS}/C_{T,TA,AS}$ values increase with increasing $pK_{a,TA}$ values between 7.5 and 9.5. Outside of this region the effect of $pK_{a,TA}$ diminishes.

The model is shown to be insensitive to the changes in the alkalinity of the water used in the absorption solution, even at high alkalinity values (Fig. 3d) due to the presence of high TA concentration (2.5 M) which serves as a strong buffer for pH changes in the absorption solution.

Figure 4 represents the sensitivity of overall model outputs to the model variables ($C_{T, TA, GM}$, $C_{T, TA, AS}$, P_{CO_2f} , and $pK_{a, TA}$). In Fig. 4a, for a TA with a p $K_{a, TA}$ of 8.54 (MDEA) and under the conditions of $P_{CO_2f} = 0.15$ atm and $C_{T, TA, AS} = 2.5$ M and $A_w = 2$ mM, the effect of TA concentration in the growth medium ($C_{T, TA, GM}$) on r_g , CUE, pH_{GM} , $C_{i, mix}$, $C_{i, GM}$, and ΔC_i are presented. As illustrated in the figure, both biomass growth rate (r_g) and the carbon dioxide utilization efficiency of the integrated system (CUE) increases

with increasing TA concentrations in the growth medium. However, while r_g increases at an increasing rate, the slope of the CUE plot start to decline for higher $C_{T, TA, GM}$ values. Since both r_g and CUE are highly sensitive to $C_{T, TA, GM}$ for a wide range of values, $C_{T, TA, GM}$ can be regarded as the most significant process parameter that should be controlled for high biomass production and carbon utilization efficiency.

In Fig. 4b, for a TA with a p $K_{a,TA}$ of 8.54 (MDEA), under the conditions of $P_{CO_2,f}=0.15$ atm, $A_{\rm w}=2$ mM, and a constant TA concentration in the growth medium ($C_{T,TA,GM}$) of 25 mM, the effect of $C_{T,TA,AS}$ on model outputs are presented. The pH in the growth medium remains constant at about 9.1 because the $C_{T,TA,GM}$ is kept constant in the growth medium. However, ΔC_i , r_g , and CUE decrease as $C_{T,TA,AS}$ is increased in the absorption solution, because the inorganic carbon concentration of the mixture ($C_{i,mix}$) entering to the microalgae bioreactor reduces due to decreasing CO_2 capture capacity, as illustrated previously in Fig. 3a.

A similar plot which depicts the effect of P_{CO_2f} on the model outputs is presented in Fig. 4c. However, as opposed to the case of $C_{T, TA, AS}$, increasing the P_{CO_2f} increases both r_g , and CUE. Especially, CUE is very sensitive to P_{CO_2f} at low CO_2 concentrations in the flue gas.

The effect of $pK_{a, TA}$ (the type of absorbing TA compound) on the model outputs is shown in Fig. 4d. In this case, pH_{GM} shows high sensitivity to this variable. The r_g and CUE profiles exhibit a maximum at different $pK_{a, TA}$ values, which correspond to tBDEA for r_g and TEA for CUE. This indicates that between these maximums there could be a certain $pK_{a, TA}$ value, i.e., a certain TA compound, where both r_g and CUE can reach their highest values simultaneously. In other words, in this integrated

Table 3 Characteristics of the tertiary alkanolamine compounds for model calculations

Compound name	Abbreviation	Structure	pKa ^a	Molecular weight (g mol ⁻¹)
triethanolamine	TEA	HO NOH	7.73	149
<i>N</i> -methyldiethanolamin e	MDEA	HO N OH	8.54	119
<i>N</i> -tert-butyldiethanolamine	<i>t</i> BDEA	t-Bu N OH	9.03	161
<i>N,N</i> -dimethylisopropanol amine	DMIPA	OH CH ₃	9.47	103

^aMeasured values at 25 °C (Rayer et al. 2014)

^bCalculated by using liquid densities of corresponding amine compound and water at 25 °C



system, for a specific $C_{T, TA, GM}$ in the growth medium for a certain TA compound (MDEA for this case), it is possible to attain significant biomass growth rates and carbon utilization efficiencies, if this $C_{T, TA, GM}$ is low enough to show no toxicity effect on microalgae growth.

It should be noted that the toxicity limitation of microalgae species for specific TA compounds $(pK_{a, TA})$ constrains the highest attainable $C_{T, TA, GM}$ value in the growth medium, which in turn directly limits the r_g and CUE, and makes the $pK_{a, TA}$ and $C_{T, TA, GM}$ the most critical parameters of the system. Thus, according to the model developed in this study, the overall efficiency of the integrated system is mostly determined by the type of TA used in the absorption solution and the maximum concentration in the growth medium of this TA compound. This could also be directly observed through the equations which were obtained by rearranging the Eqns 17 and 18 for the conditions created in the sensitivity analysis (see the supplementary material in Appendix A).

Model Predictions

The model predictions, given in Fig. 5, are based on the effect of the total concentration of TA in the growth medium

 $(C_{T, TA, GM})$ on main model outputs, r_g and CUE, since $C_{T, TA, GM}$ was determined to be the most significant process parameter that should be controlled for high biomass production and carbon utilization efficiency (Fig. 4a).

The model predictions for different TA compounds are presented in Fig. 5a, for $C_{T, TA, AS} = 2.5$ M, and $P_{CO_2, f}$ = 0.15 atm. The $r_{\rm g}$ and CEU increase with increasing $C_{T. TA. GM}$, as expected. The r_g also increases when the pK_a value of the TA compound increases, except for DMIPA and tBDEA, which result in similar growth rates for the same growth medium concentrations, despite DMIPA having a higher pK_a value than tBDEA. This is because beyond a certain p K_a value, ΔC_i starts to decrease, which in turn reduces the daily growth rate, as shown in (Fig. 4d). The highest relative increase with respect to r_a occurs for MDEA, compared to tBDEA and DMIPA. As opposed to the effect on r_{o} , the CEU decreases proportionally with increasing pK_a value of the TA compound. This could arise from the increase in $C_{i,GM}$ when the pK_a of the absorption compound increases (Fig. 4d). The model reveals that the use of MDEA as the CO2 absorbing chemical could provide relatively high microalgae growth rates without significant loss in carbon utilization efficiencies compared to other selected TA compounds. For a given set

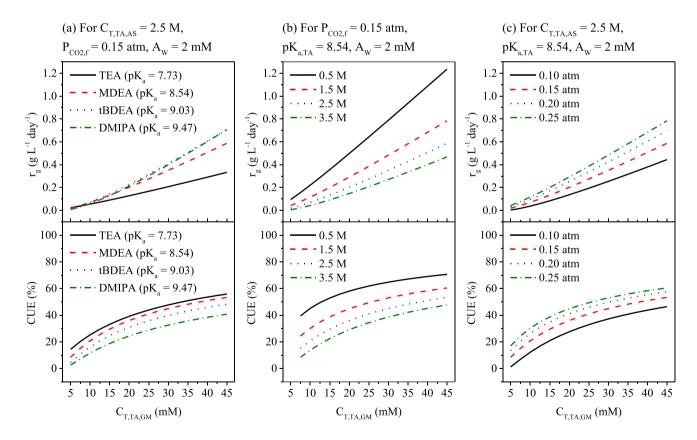


Fig. 5 Comparison of the model results as a function of tertiary alkanolamine concentration in the growth medium for different **a** tertiary alkanolamine compounds, **b** tertiary alkanolamine concentrations in the absorption solution, and **c** partial pressures of CO₂ in the flue gas



of process parameters ($C_{T,TA,AS}$ and P_{CO_2f}) and for a given range of MDEA concentrations in the growth medium, the model estimated an r_g between 0.02 and 0.5 g L⁻¹ day⁻¹, and a CUE between 9 and 50%. These r_g values projected by the model correspond to 4–100 g m⁻² day⁻¹ of biomass production rates for a typical open raceway pond system, having a water depth of 0.2 m. The biomass production rate in raceway ponds is reported to be typically around 15 g m⁻² day⁻¹ (Williams and Laurens 2010). Therefore, it is plausible to assume that the CO₂ requirement of a typical raceway pond can be fulfilled by an integrated system using MDEA as the CO₂ absorber, even for low MDEA concentrations in the growth medium.

In Fig. 5b, the parameter varied is the TA concentration in the absorbing solution ($C_{T,TA,AS}$) from 0.5 to 3.5 M for the TA compound with the pK_a of 8.54 (MDEA) and $P_{CO_2,f}$ of 0.15 atm. Higher r_g and CUE values are obtained at lower $C_{T,TA,AS}$ values, as also presented in Fig. 4b. About 2.6- and 1.7-fold average increases, respectively, in the r_g and CUE are estimated by the model when the MDEA concentration in the absorption solution is lowered by 80%.

In Fig. 5c, r_g and CUE are presented for different P_{CO_2f} from 0.1 to 0.25 atm. The results indicate that higher CO_2 contents in the flue gas will provide higher biomass production rates and carbon utilization efficiencies. For a 60% increase in P_{CO_2f} (from 0.15 to 0.25 atm), the model predicts 50% and 30% average increases in r_g and CUE, respectively. Although, using lower MDEA concentration in the absorption solution and/or increasing CO_2 content of the flue gas will greatly benefit r_g and CUE, it is important to consider that these kinds of adjustments in these operating parameters require certain modifications in existing CO_2 capture facilities—even in alternative combustion techniques (e.g., oxy-fuel combustion).

It is worth mentioning again that the model results are constrained by the maximum TA concentration ($C_{T, TA, GM}$) beyond which microalgae growth starts to reduce due to toxicity of the TA. This maximum concentration must be determined experimentally under inorganic carbon-limited conditions in order to obtain growth kinetics constants (μ_{max} and K_{Ci}) and hence to estimate biomass production rates more accurately. In addition, because of the assumption of complete equilibrium in both the absorption solution and the growth medium, the application of the model to real case scenarios may produce overestimated results. Thus, the model results must be regarded as a guide to estimate which chemical absorber or absorbers could be worth investigating in detail for integration of conventional amine-based CO_2 capture systems with microalgae cultivation systems.

Conclusions

According to the model developed in this study, the efficiencies of biomass growth and carbon utilization in the integrated system are determined mainly by the type (pK_a value) and the concentration of the tertiary alkanolamine in the growth medium. The alkanolamine concentration in the absorption solution and the CO₂ content of the flue gas are also critical parameters that control the performance of the system. If the growth characteristics of microalgae species are determined in an alkanolamine solution, this model can be used to evaluate different operation alternatives for optimum performance of an integrated CO₂ absorption microalgae production system. For such cases, the model can serve as a useful decision-making tool. The model reveals that, among the four types of tertiary alkanolamine selected in this study, MDEA could be more favorable as a CO₂ absorber than the others in terms of providing high biomass productivities and high carbon dioxide utilization efficiencies. However, further studies are required to reveal how well MDEA could serve as a CO₂ transporter to microalgae cultivation system without affecting the growth conditions of microalgae species.

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Data Availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of Interest The authors declare no competing interests.

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