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Kinetic modelling of microalgae cultivation for wastewater treatment and carbon dioxide sequestration

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ABSTRACT

A simple and robust microalgae kinetic model has been developed for application in the prediction and control of algae cultivations in wastewater. The microalgae kinetic model was calibrated using experimental cultivation data from *Desmodesmus* sp. to determine specific microalgae growth rates (μ_{max} and μ_{maxNO3}), microalgae death rates (μ_d), and the NH_4^+ to NO_3^- oxidation rate (μ_B). Model parameters obtained were: $\mu_{max} = 0.17\ day^{-1}$, $\mu_d = 0.004\ day^{-1}$, and $\mu_B = 0.14\ day^{-1}$. Microalgae specific growth rate based on NO_3^- alone ($\mu_{maxNO3} = 0.1\ day^{-1}$) was lower than the overall growth rate (μ_{max}). The kinetic model was validated using additional experimental data for the *Desmodesmus* sp. and *Scenedesmus obliquus* cultivation in wastewater containing 0% and 7% landfill leachate, with accuracy above 98% in all cases. These results demonstrated the kinetic model was accurate in predicting microalgae growth, wastewater nutrient removal, and changes in the culture media pH. Biomass productivity of the algae culture was associated with an exponential increase in the media pH, which led to ammonia volatilisation and decreased carbon intake. Between 28.8 and 29.7% of the initial NH_4^+ was lost to ammonia volatilisation in wastewater containing 7% landfill leachate. Hence, loss of ammonium nitrogen contained in domestic wastewater must be avoided to ensure steady and efficient inorganic carbon utilisation which inherently maximises biomass production efficiency. The optimal pH for the microalgae culture was 8.1, at which point microalgae could achieve about 99% carbon fixation efficiency. To ensure constant pH in the microalgae growing system, immediate removal of the OH^- generated is needed, which could be facilitated by injections of 1.14 g CO_2 and 0.067 g OH^- per gram of produced algae when using NH_4^+ nutrient, and 1.54 g of CO_2 per gram of produced algae when using NO_3^- nutrient. This could be done in a wastewater pond by using an optical density-controlled smart CO_2 injection system.

1. Introduction

Disposal of wastewater without treatment often results in eutrophication, an excessive enrichment of the water body with nutrients which leads to algal blooms, and more long-term problems of heavy metals contamination [1,2]. Eutrophication has become a widespread and serious environmental concern since the mid-20th century, with about 48% of lakes and reservoirs in North America, 54% in Asia and the Pacific, 53% in Europe, 41% in South America, and 28% in Africa being affected by eutrophication [2]. In Mexico only 57% and 32% of the total municipal and industrial wastewater generated in the country is treated [3], therefore, eutrophication has had a great impact in receiving water bodies because of the discharges of untreated wastewater. These deleterious environmental consequences can be avoided through carbon-neutral wastewater treatment using microalgae. An integrated microalgae-based process would lead to reductions in greenhouse gas emissions, production of usable microalgae biomass and low-cost water treatment [4]. However, the major challenge is an adequate understanding of the kinetics of microalgae growth in wastewater, to allow for optimal design and operation of ponds for wastewater treatment.

Microalgae cultivation is a promising approach for simultaneous CO_2 conversion and wastewater treatment. Microalgae autotrophic growth utilises inorganic carbon in the form of dissolved CO_2 in the bicarbonate-carbonate buffer system ($CO_2(aq) - HCO_3^- - CO_3^{2-}$) [5,6]. Previous studies have shown that CO_2 fixation efficiency, when injected continuously in microalgae culture, was in a range of 4–66% at input CO_2 concentration of 6–15% for *Scenedesmus* sp. [7–10], and 16–64% at an input CO_2 concentration of 1–15% for *Chlorella* sp. [8,11–13]. Within these CO_2 fixation yields, microalgae have reported growth rates between 0.19 and 1.24 d^{-1}. Although no specific value for

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CO_2 fixation efficiency was provided in the literature aforementioned, it was observed that the higher amount of CO_2 the lower CO_2 fixation efficiency due to the loss of CO_2 through outgassing. Therefore, controlled-dosing of CO_2 to match the inorganic carbon demand of the microalgae culture media may be required to minimise the outgassing of CO_2. It has been reported that CO_2 fixation efficiency increased from 64% when added continuously, to about 95% when intermittently injected into *Chlorella vulgaris* culture media [13]. Apart from inorganic carbon which could be obtained from CO_2 dissolved in water, the aquatic medium must contain sources of inorganic nitrogen, phosphorus, and iron for autotrophic microalgae growth [5,14]. Silica would also be required by many chrysophytes, such as golden algae (*Chrysophyceae*) and diatoms (*Bacillariophyceae*), as a nutrient for their cell walls [15,16]. From these, inorganic nitrogen and phosphorus are the two major nutrients required for microalgae cultivation [5,14]. The most important being nitrogen, as it constitutes about 1–10% weight of the algae biomass [5]. Microalgae require less phosphorus for their growth compared to inorganic carbon and nitrogen sources, with its content typically < 1% of the algae biomass [5,14]. Microalgae have been shown to effectively utilise the levels of nitrogen (2–1960 mg/L) and phosphorus (1–117 mg/L) found in different types of wastewater, sometimes even coupled with the biofixation of toxic metals [2,17,18]. Nitrogen sources commonly used are ammonium, nitrate, and urea. Ammonium is the most preferred because its assimilation requires less energy [17]. Ammonium exits in equilibrium with ammonia depending on the culture pH, with free ammonia concentration increasing with the pH [19,20]. High concentrations of free ammonia have been found toxic and reported to inhibit growth to most strains of microalgae, hence effluents with high ammonium nitrogen concentration (e.g. landfill leachate) need previous dilution [17,21]. Other shortcomings of the ammonia nitrogen source are volatilisation of ammonia, which has been reported in ammonium-rich aqueous media at pH above neutrality [19,22], and its reduction to nitrate by autotrophic bacteria [23].

Studies have shown that growth kinetics of microalgae are dependent on the availability of sources of inorganic carbon, nitrogen and phosphorus; plus light intensity and media temperature, [24–27]. For microalgae growth at constant light intensity, temperature, and homogenous mixing; usually substrate and nutrients availability determine the rate of the algae biomass accumulation. Microalgae growth kinetic models give an insight into the algae biomass production and the nutrient consumption rate, providing essential data for the design of ponds for high efficiency algae cultivation. A robust microalgae kinetic model is very crucial in prediction of nutrients removal, biomass growth, and optimisation of operating conditions for algae cultivation in wastewater. Among the kinetic models that have been used to study microalgae growth, the most favoured mathematical models are the Monod and Droop models, which are usually applied in studies of the specific growth rates of microalgae as a function of one of the three major substrates – inorganic carbon, nitrogen, or phosphorus [17,28–30]. Generally, the growth rates of organisms in both Monod and Droop models could be limited by the availability of any of the substrates as soon as its concentration becomes negligibly low. Hence, nutrient limitation can determine the maximum rate of microalgae growth, and this can be described using the Monod-type kinetics in Eq. (1), or Droop model [27,31], in Eq. (2). The maximum specific growth rate ($\mu_{m,\ D}$) in the Droop model equation is the specific growth rate of the algae at an infinite internal nutrient cell content (also called cell quota). The μ_m in the Monod equation is the maximum growth rate at infinite external nutrient concentration. Therefore, the Monod and Droop models can be related by Eq. (3).

$$\mu_m = \mu_{max} * \frac{[A]}{K_A + [A]} \tag{1}$$

$$\mu_D = \mu_{D,max} * \left(1 - \frac{Q_0}{q}\right) \tag{2}$$

$$\mu_{D,max} = \frac{\mu_m \rho_m}{\rho_m - \mu_m Q_0} \tag{3}$$

where:

μ_m: Monod specific growth rate (time^{-1}); μ_D: Droop specific growth rate (time^{-1}); μ_{max}: Monod maximum specific growth rate (time^{-1}); $\mu_{m,D}$: Droop maximum specific growth rate (time^{-1}); K_A: half-saturation constant for nutrient A (mg/L); [A]: concentration of the nutrient A (mg/L); Q_0: minimum cell quota; q: cell quota; ρ_m: maximum nutrient uptake rate per cell.

Notwithstanding existing studies showing that the Droop model can accurately reproduce the dynamics of microalgae growth in a constant environment [31,32], this model is still not widely used by researchers compared to the Monod model [26,27]. The Monod model is commonly used because the external nutrient concentration in the culture media can be easily measured. Although microbial growth rates are more accurately determined by the internal cellular nutrient contents than on the concentration measured externally in the culture media [5], it is difficult to experimentally measure the cell quota of microalgae species, which limits the Droop model utilisation.

The Monod model in Eq. (1) is generally used to study microalgae growth that is limited by a single nutrient. The model does not take into considerations multiple-nutrient limited growth although existing studies have shown that two or more substrates could limit microbial growth rates [5,33]. This decreases the accuracy of specific growth rates predicted for microalgae limited by more than one substrate during cultivation. In such cases, the Monod model could be extended to explain dual nutrient limited growth of microalgae [25] as in Eq. (4), and also include carbon limitation as in Eq. (5).

$$\mu = \mu_{max} * \frac{[A]}{K_A + [A]} * \frac{[B]}{K_B + [B]} \tag{4}$$

$$\mu = \mu_{max} * \frac{[C]}{K_c + [C]} * \frac{[N]}{K_N + [N]} * \frac{[P]}{K_P + [P]} \tag{5}$$

In a complex culture media, like wastewater, microalgae growth could be dependent on the concentrations of main nutrients and carbon. Therefore, a Monod model as in Eq. (5), for the autotrophic growth of algae, considering inorganic carbon, nitrogen and phosphorus sources as limiting, could be used to explain microalgae growth kinetics [34,35].

The aim of this study is to develop a robust kinetic model that simulates microalgae growth in wastewater when limited by more than one substrate (inorganic carbon, nitrogen or phosphorous), incorporating the effects of NH_3 volatilisation, oxidations of the ammonium nitrogen to nitrate by autotrophic bacteria, and the inherent changes of pH in the culture media. With this, the model would predict CO_2 sequestration, and nutrient removal as a dual process of microalgae cultivation and wastewater treatment. The model will be calibrated and validated using experimental data from cultivations of microalgae in wastewater, in some cases, with added landfill leachate. This model development is an important step in predicting the performance of microalgae cultivation in wastewater ponds.

2. Materials and methods

2.1. Procedure for the microalgae cultivation in wastewater

Wastewater used for the microalgae cultivation was obtained from the Wastewater Treatment Plant (WWTP) at Cerro del Agua, located in Ciudad Universitaria (UNAM), México. The wastewater was collected in 20 L containers, filtered to remove suspended solids (Filter with 8 μm pore size), and stored at 4 °C. The wastewater had initial pH in the range of 8.0–8.5, 102.66 ± 1.68 mg/L ammonium nitrogen, 1.8 ± 1.3 mg/L nitrate, 25.60 ± 1.14 mg/L orthophosphate, and total inorganic carbon measured as alkalinity value (280 mg/L as $CaCO_3$).