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Mitigation of inhibition effect of acid gases in flue gas using trona buffer for autotrophic growth of *Nannochloris* sp

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ABSTRACT

In this study, trona buffer was used to mitigate the previously reported inhibition effect of CO_2, SO_2, NO, and HCl gases in combustion flue gases for the growth of *Nannochloris* sp. Culture medium with trona buffer after absorbing CO_2(g) contains high dissolved inorganic carbon (DIC) concentration that can help maximize the growth and alleviate the inhibition effect as long as the pH of the medium is controlled at an optimum pH (pH ~7–8) window for the growth of *Nannochloris* sp. A supply of high purity CO_2(g) did not inhibit the growth. The acid gaseous constituents including SO_2, NO, and HCl gases did not significantly reduce the growth as compared to the results previously reported. This study suggests that trona buffer can be effectively used for microalgae cultivation as biological CO_2 remediation when it is considered being integrated into a coal-fired power plant after wet flue gas desulfurization system.

1. Introduction

Carbon dioxide (CO_2) is one of the main contributors (more than 75%) to climate change [1]. As an increase in human activities, the CO_2 concentration in atmosphere has reached 404.02 ppm in February 2016 that is reported to exceed a safe upper limit (350 ppm) [2,3]. According to the U.S. Environmental Protection Agency, ~37% of entire CO_2 emissions in the U.S. were produced from the combustion of fossil fuels to generate electricity in 2013 [4]. Plants can convert CO_2 gas (CO_2(g)) into organic matter and store in the forms of carbohydrate, protein, and lipids by photosynthesis for diverse applications and products [5–7]. In this context, an interest in microalgae has recently increased due to fast growth (approximately 3 times faster than terrestrial plants) using CO_2, a fair amount of lipids, and high heating values for potential use of carbon cycle and energy recovery [8–12].

In microalgae cultivation processes, bubbling air is conventionally used to supply dissolved inorganic carbon ($DIC=HCO_3^- + CO_2(aq)$) for the autotrophic growth. However, atmospheric CO_2(g) concentration is not high enough to generate the DIC concentration in culture medium for fast growth in engineered cultivation systems. However, it was reported that microalgal growth was significantly inhibited when CO_2(g) concentration was higher than 5% and thus CO_2(g) diluted with air was used in many previous studies [13–17].

Biological CO_2 conversion via autotrophic microalgae cultivation could be a good option for reducing risk and offsetting the cost of carbon capture and sequestration. Coal combustion flue gas typically comprises of ~10–16% of CO_2 [13]. Therefore, direct use of the flue gas for the growth of microalgae can greatly reduce the cost for the separation and purification of CO_2. However, the growth of microalgae was reported to be inhibited by other gaseous components in flue gas, such as NOx (100–300 ppmv) and SOx (230–320 ppmv) [13]. When a coal-fired power plant is equipped with SO_2 and NOx control devices, these two concentration ranges are high enough to cover their maximum concentrations in the flue gas. According to previous studies, SO_2 and NO significantly inhibited the growth rate of microalgae by lowering the pH of the culture medium [13,17]. Therefore, sodium hydroxide (NaOH) was previously used to control the pH when high CO_2 and acid flue gas components were present in flue gas [17,18]. However, it was reported that this method was effective only for some strains, such as *Chlorococcum littorale* and *Chlorella KR-1* [17,18].

In this study, trona ($Na_3(CO_3)(HCO_3)\cdot 2H_2O$) was used as a buffer chemical to minimize the inhibition effect of CO_2, SO_2, NO, and HCl gases. Trona is a naturally-occurring mineral and comprises of sodium bicarbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3) at a 1:1 molar ratio. Trona is also inexpensive compared to other sodium-based buffer chemicals such as $NaHCO_3$ and Na_2CO_3 (trona: $0.10/lb; industrial grade $NaHCO_3$: $0.46/lb; industrial grad Na_2CO_3 $0.55/lb). Trona has high solubility in water (120 g/L at 0 °C,

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157 g/L at 20 °C), and the solution can generate high DIC concentrations after CO_2(g) absorption. In our previous study, *Chlorella vulgaris* could successfully grow using high purity CO_2(g) (>99%) in conjunction with $NaHCO_3$ buffer [11]. Therefore, it is expected that the inhibition effect of the gases may be reduced when trona is used for the growth of microalgae.

Nannochloris sp. has been selected for this study because *Nannochloris* sp. is reported to contain a large amount of lipids (25–56% dry wt.) [19–21]. In addition, the mitigation effect of trona buffer on SO_2 and NO gases can be compared with the previous results reported with the inhibition effect of 400 ppmv SO_2 and 300 ppmv NO gases on the growth of *Nannochloris* sp. [20]. An optimum trona concentration (0.02 M) that did not inhibit the growth rate of *Nannochloris* sp. was determined for this study. Therefore, a main objective of this study is to investigate the mitigation effect of trona buffer without a need for its continuous addition on the inhibition effect of CO_2, SO_2, NO, and HCl gases in coal combustion.

2. Materials and methods

2.1. Culture medium and conditions

Nannochloris sp. used (LB1999) in this study was purchased from UTEX Culture Collection of Algae at the University of Texas at Austin (UTEX). A trona sample used in this study ($Na_3(CO_3)(HCO_3)\cdot 2H_2O$, T200, purity: 90–98%) was provided by Solvay Chemicals, Inc. A 3.5-L culture medium was prepared by following the modified Shuisheng-4 medium (SH4 M) in a 4 L-cylindrical bottle (24 cm (height) × 14 cm (diameter)) and 0.02 M (4.5206 g/L H_2O) of trona was added to the medium. Here, 350 mL of the modified SH4 M in a 400-mL cylindrical bottle was separated before adding trona for a culture without trona (S0).

Then *Nannochloris* sp. was inoculated in the medium. After inoculating the initial cell density of *Nannochloris* sp. in the SH4 M medium was found to be 168.0 ± 0.1 mg/L 350 mL of the prepared SH4 M medium was added to each eight 400-mL cylindrical bottles. After preparing the cultures, the pH of the cultures was daily controlled at 7.4 by bubbling simulated flue gases with different compositions including S0-S4, N1-N4 and H1-H4: S0 (CO_2 = 100%, N_2 = 0%, SO_2 = 0 ppmv, NO = 0 ppmv, HCl = 0 ppmv), S1 (=N1 = H1) (CO_2 = 100%, N_2 = 0%, SO_2 = 0 ppmv, NO = 0 ppmv, HCl = 0 ppmv), S2 (=N2 = H2) (CO_2 = 12%, N_2 = 88%, SO_2 = 0 ppmv, NO = 0 ppmv, HCl = 0 ppmv), S3 (CO_2 = 12%, N_2 = 88%, SO_2 = 50 ppmv, NO = 100 ppmv, HCl = 0 ppmv), S4 (CO_2 = 12%, N_2 = 88%, SO_2 = 50 ppmv, NO = 300 ppmv, HCl = 0 ppmv), N3 (CO_2 = 12%, N_2 = 88%, SO_2 = 50 ppmv, NO = 100 ppmv, HCl = 0 ppmv), N4 (CO_2 = 12%, N_2 = 88%, SO_2 = 50 ppmv, NO = 300 ppmv, HCl = 0 ppmv), H3 (CO_2 = 12%, N_2 = 88%, SO_2 = 50 ppmv, NO = 300 ppmv, HCl = 0 ppmv), and H4 (CO_2 = 12%, N_2 = 88%, SO_2 = 50 ppmv, NO = 300 ppmv, HCl = 10 ppmv). The compositions of individual gaseous components in a simulated flue gas were controlled by individual mass flow controllers. During the culture, all of the cultures were mixed by using magnetic stirrers at a speed of 550 rpm to suspend *Nannochloris* sp. cells. The mixing speed was found to be enough to homogenize microalgal cells inside the reactor based on our previous study [11].

During the culture, fluorescent lamps with 6500 K color temperature were used as a light source. The incident light intensity at the reactor surface was set to 257.0 ± 11.7 μmol/(m^2 s), and a 16-h light and 8-h dark cycle was applied to all the cultures.

2.2. Determination of cell mass density of Nannochloris sp

The cell mass density of *Nannochloris* sp. in the culture medium was determined by measuring the optical density at 750 nm every

Table 1
Experimental data to determine the photosynthetic efficiency (%) in terms of CO_2, N_2, SO_2, NO, and HCl concentrations.

Name		CO_2 (%)	N_2 (%)	SO_2 (ppmv)	NO (ppmv)	HCl (ppmv)	Total dry Biomass (g/(L·12d))	Incident Light Intensity (μmol/(m^2 s))	A/V (1/m)[a]	Growth Yield, Y (g/kJ)	Photosynthetic Efficiency (%)
S1	N1	H1	100	0	0	0	3.41	256.95	57.31	8.98×10^{-4}	1.98
S2	N2	H2	12	88	0	0	3.39	256.95	57.31	8.94×10^{-4}	1.97
S3			12	88	100	50	3.14	256.95	57.31	8.24×10^{-4}	1.81
S4			12	88	300	50	2.77	256.95	57.31	7.23×10^{-4}	1.59
	N3		12	88	50	100	0	3.23	256.95	57.31	8.49×10^{-4}	1.87
	N4		12	88	50	300	0	3.15	256.95	57.31	8.26×10^{-4}	1.82
		H3	12	88	300	300	0	3.20	256.95	57.31	8.40×10^{-4}	1.85
		H4	12	88	300	300	10	2.88	256.95	57.11	7.54×10^{-4}	1.73

The pH of all cultures was controlled at 7.4 once daily.
[a] A/V = ratio of surface area (A) of bottle to volume of culture medium (V).