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Carbon dioxide sequestration from industrial flue gas by *Chlorella sorokiniana*

Kanhaiya Kumar, Debopam Banerjee, Debabrata Das *

Department of Biotechnology, Indian Institute of Technology Kharagpur, West Bengal 721302, India

HIGHLIGHTS

- CO_2 sequestration from flue gas of oil producing company using *Chlorella sorokiniana*.
- Techniques for minimizing inhibitory effect of high concentration of CO_2 and H_2S.
- Comparison of fatty acids composition of pure CO_2 and flue gas sequestered biomass.
- Flue gas caused increase in fatty acids chain length and degree of unsaturation.
- Flue gas caused synthesis of some additional pigments and metabolites.

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ABSTRACT

The present study investigated the feasibility of using *Chlorella sorokiniana* for CO_2 sequestration from industrial flue gas. The flue gas emitted from the oil producing industry contains mostly CO_2 and H_2S (15.6% (v/v) and 120 mg L^{-1}, respectively) along with nitrogen, methane, and other hydrocarbons. The high concentration of CO_2 and H_2S had an inhibitory effect on the growth of *C. sorokiniana*. Some efforts were made for the maximization of the algal biomass production using different techniques such as diluted flue gas, flue gas after passing through the scrubber, flue gas passing through serially connected photobioreactors and two different reactors. The highest reduction in the CO_2 content of inlet flue gas was 4.1% (v/v). Some new pigments were observed in the flue gas sequestered biomass. Fatty acid composition in the total lipid was determined to evaluate its suitability for food, feed, and biofuel.

1. Introduction

The threat of global warming is becoming severe because of increasing CO_2 concentration in the atmosphere. In 2011, the rate of increase in atmospheric CO_2 was 1.94 ppm/year; more than twice the estimated value in 1959. Presently, CO_2 is contributing nearly 52% in total global warming (Velea et al., 2009). Biological CO_2 sequestration from flue gas is gaining attention because of its eco-friendly and cost effective nature (Kumar et al., 2013, 2011). Use of algae for CO_2 sequestration has multiple advantages. Photosynthetic efficiency of microalgae is nearly 10 times greater than that of terrestrial plants (Skjanes et al., 2007). In addition, they are the source of renewable energy and their biomass can be utilized for the production of high value products. Algae can grow in open pond as well as in closed photobioreactors. The advantages of closed photobioreactors are high productivity, easy operation, better control over physiochemical parameters, and sterile operation. Airlift and bubble column photobioreactors have wide acceptance for algal cultivation because of their simplicity in gas–liquid contacting application (Kastanek et al., 2010). Airlift bioreactor is of special interest because of higher mass transfer, regular light and dark cycle, low and homogeneous shear stress to the cells (Kumar and Das, 2012; Vunjak-Novakovic et al., 2005).

CO_2 sequestration by biological means is limited only to laboratory-scale using air–CO_2 gas mixture. Till today, very scarce *in situ* research is available on algal cultivation using flue gas. Component and composition of flue gas vary with the source of its generation. High temperature, presence of toxic gases like NO_x, SO_x, H_2S, and particulate matters of flue gas are also creating problems in operation for CO_2 sequestration using algae. Flue gas components cause acidification to the medium and poses environmental stress to algae. Some of the sources of flue gas used for cultivation of algae are incineration units (Kastanek et al., 2010), coal fired thermal power plant (Maeda et al., 1995), and fossil fuel fired plant (Zeiler et al., 1995). The algae such as *C. vulgaris* BEIJ 1890 (Kastanek et al., 2010), *Chlorella* sp. T1 (Maeda et al., 1995), *M. minutum*

* Corresponding author. Tel.: +91 03222 278053; fax: +91 3222 255303.
E-mail addresses: ddas@hijli.iitkgp.ernet.in, ddas.iitkgp@gmail.com (D. Das).

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(Zeiler et al., 1995), *Tetraselmis* sp. (Matsumoto et al., 1995) are mostly used for this purpose.

Previously, continuous supply of flue gas into the culture was found to have an inhibitory effect on the growth of the algal cells (He et al., 2012). Therefore, isolation of SO_x, NO_x tolerant algae, the addition of $CaCO_3$ to maintain pH near to 7, controlling the pH drop by addition of NaOH were some of the strategies adopted to overcome the flue gas inhibition on the growth of the microalgae (Jiang et al., 2013; Westerhoff et al., 2010). However, SO_x and NO_x tolerant algae were effective only at lower concentrations of these acidic gases whereas neutralization with NaOH was costly and caused undesirable effects on algae due to high ionic strengths. Recently, on–off pulse of flue gas was adopted by some of the researchers to overcome the flue gas inhibition on algal cells (He et al., 2012; Jiang et al., 2013; Chiu et al., 2011). He et al. (2012) reported frequency of 10 s on-time and 5–9 min off-time as an effective strategy for overcoming high CO_2 stress. However, employing this strategy required continuous stirring of the culture for mixing and sophisticated instrument to control the frequency of the flue gas injection.

Chlorella sp. grows much quicker and considered as algal weed because of its ability to survive under harsh and high oxidizing environmental conditions. It is also known as a good source of carbohydrates, lipids, proteins, and vitamins. The algal biomass can be used as raw material as single cell protein for human consumption (Mahasneh, 1997) or as feed for fish in aquaculture systems (Hamasaki et al., 1998). Moreover, the physiological response to high CO_2 concentration may give rise to several useful metabolites and pigments. Previously, carotenoids have been shown to protect algal cells from photooxidative damage (Siefermann-Harms, 1985). The carotenoids (such as astaxanthin, canthxanthin, lutein, and β-carotene) have significant commercial importance. It has also been reported that carotenoids may inhibit carcinogenesis due to their antioxidant activity. Milbemycins β are a group of macrocyclic lactones with a highly potent antiparasitic activity (Prichard, 2005) besides having anthelmintic and insecticidal properties. Pregnan-20-one is a neuroactive steroid which plays a vital role in stress, pregnancy, and CNS neurotransmission (Khisti et al., 2003). These kinds of compounds can be used to aid neurogenesis and epileptic disorders. Further, fatty acids produced from algae have nutritional, biofuel, and pharmaceutical properties. For example, oleic acid has a positive effect on cardiovascular diseases and lowers cholesterol level (Beyhan et al., 2011) whereas lauric, palmitic, linoleic, oleic, stearic, and myristic acids have antibacterial and antifungal properties (Agoramoorthy et al., 2007). In addition, lauric acid is used for manufacturing of cocoa butter, flavourings, alkyd resins, soaps, shampoos, and other surface active agents, including special lubricants. Eicosenoic acid (C20:1) and erucic acid (C22:1) have usefulness in cosmetic products as they provide a protective layer over the skin. Similarly, tricosanoic acid (C23:0) is used in the food and beverage industry.

The main objective of the present research work was to determine in-field feasibility of *C. sorokiniana* for sequestrating CO_2 from flue gas. It also aimed to study the effect of stress conditions induced by flue gas on pigments and fatty acid composition.

2. Methods

2.1. Microalgae and culture medium

The culture of *C. sorokiniana* was obtained from Dr. Kari Skjanes (Bioforsk, Norway). Modified TAP (-acetate) medium was used in all experiments (Kumar and Das, 2012). All the experiments were conducted at field condition where temperature was found to vary from 25 to 40 °C. Airlift and bubble column photobioreactors were designed and fabricated as described by Kumar and Das (2012). The volume of both airlift and bubble column reactors were 1.4 L. The rate of flow of gas into the reactor was 0.33 vvm. Culture was constantly illuminated with cool white fluorescent tubes. Light intensity falling on the surface of reactor from one side was measured approximately 120 μmol m^{-2} s^{-1} as measured with a quantum meter (LX-101, Lutron, Taiwan).

2.2. Scrubber

A slurry of zinc oxide (ZnO) of 6.25 g L^{-1} was used as a scrubber for removing the H_2S present in the flue gas. In order to ensure continuous mixing of the slurry, Bubble column reactor was used as a vessel. Zinc oxide reacts with hydrogen sulfide and makes zinc sulfide and water as shown in the following Eq. (1).

$$ZnO(s) + H_2S(g) \rightleftharpoons ZnS(s) + H_2O(g). \quad (1)$$

2.3. Gas analysis

Flue gas of oil producing industry was used in the present study. Gas composition was analyzed by GC (Agilent) using a thermal conductivity detector (TCD) with N_2 as a carrier gas. The gas composition of inlet flue gas was 15.65% (v/v) carbon dioxide, 72.79% (v/v) nitrogen, 0.02% (v/v) hexane, 10.63% (v/v) methane, 0.54% (v/v) ethane, and 0.36% (v/v) other hydrocarbons. H_2S was measured separately using a piston type hand pump that was used to draw a fixed volume of the gas through a calibrated glass tube filled with lead acetate.

2.4. Dry weight, biomass productivity, and net specific growth rate determination

Optical density (OD) of cells was determined in a spectrophotometer at 682 nm (Chemito). Dry cell weight (Dwt) was calculated using a calibration plot between Dwt and OD. Carbon present in dry cell weight of microalgae was assumed as 50% (w/w) which corresponds to a requirement of 1.83 g of CO_2 for the production of 1 g dry cell weight of microalgae (Kumar and Das, 2012). The overall biomass productivity $P_{overall}$ (g L^{-1} d^{-1}) in the batch was calculated using the following Eq. (2).

$$P_{overall} = \frac{\Delta X}{\Delta t} \quad (2)$$

Net specific growth rate, μ_{net} (d^{-1}) was calculated from Eq. (3)

$$\mu_{net} = \frac{\Delta \ln X}{\Delta t} \quad (3)$$

where ΔX and $\Delta \ln X$ are the total amount of biomass and difference of natural logarithmic biomass of initial and final cultivation time, respectively with total cultivation time of Δt (Kumar and Das, 2012; Jiang et al., 2013).

2.5. Growth kinetics using logistic equation

Logistic equation was used to determine the growth kinetics of algae. It can explain the entire growth profile (lag, exponential, and stationary phase) without taking substrate consumption into consideration (Kumar and Das, 2012). The following is the logistic Equation.

$$\frac{dC}{dt} = K_c\, C\, (1 - \frac{C}{C_{max}}) \quad (4)$$

where C, C_{max}, and K_c are the dry cell weight (g L^{-1}), maximum dry cell weight (g L^{-1}), and apparent specific growth rate (d^{-1}). On integration and rearrangement, Eq. (4) takes the form of Eq. (5)