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Oil & Natural Gas Corporation Ltd. (ONGC)

Report on lab-scale experiments on CO_2 uptake by microalgae cultivation for CO_2 capture at Hazira plant

ccsp
Carbon Capture and Storage Program

Introduction:

At ONGC plant, Hazira, 43 million cu.m / day of sour gas containing 150 ppm of H_2S is handled. The sour gas is sweetened and the H_2S concentration is brought down to less than 4 ppm H_2S. In the process vent gas is released which contains on an average 23% CO_2, 15% O_2 and 60% N_2. The proposed project focuses on carbon dioxide sequestration using algae. The experiments were carried out from April 15th 2014 till October 15th 2014 and the detailed report is given below.

Algae have recently received a lot of attention as a new biomass source for the production of renewable energy. Some of the main characteristics which set algae apart from other biomass sources are that algae (can) have a high biomass yield per unit of light and area, can have a high oil or starch content, do not require agricultural land, fresh water is not essential and nutrients can be supplied by wastewater and CO_2 by combustion gas or vent gas as it is in Hazira plant's case. The focus of this project was on carbon dioxide sequesteration and in conversion of CO_2 to value added products, by combination of microalgal biomass production and anaerobic digestion for biogas generation.

Flue gases / vent gases are a resource yet to be fully utilized in microalgal biotechnology, not only to moderate the anthropogenic effects on our climate, but also to steer microalgal resource management towards innovative applications of microalgal biomass compounds (Hende et al 2012). Globally several algal pilot reactors with injection of flue gas have been and are being constructed (Aquafuels 2011). Israel Electric Company and Seambiotic Ltd inject flue gas into open ponds with *Nannochloropsis* cultures (Christenson & Sims, 2011). In Hawaii, Cyanotech Corporation uses a patented system to provide flue gas to *Arthrospira* sp. Cultures and to recover the heat of the fossil fuel engine to dry the cyanobacteria (Cyanotech corporation, 1997). The following objectives were agreed upon to demonstrate at a pilot scale, the sequesteration of carbon dioxide and biogas production from algae produced.

Objectives:

The Specific objectives of this project are

A - Screening of microalgae

B - Correlation between maximum methane potential and microalgae

C - Lab scale demonstration of carbon dioxide sequesteration using microalgae

The tasks under the above mentioned objectives are as follows

	Tasks
1)	Reactor construction and algal strain/strains selection
2)	Installation of reactor and pre test
3)	Establishing the protocol and experimental CO_2 sequestration studies
4)	Biomethanation potential of algae and pilot scale studies of biogas production from algae
5)	completion of the project

Reactor construction:

A pilot high rate pond reactor for algal growth with a useful volume of 0.2 m^3 was constructed with a paddle wheel. A carbon dioxide (CO_2) absorption column with a volume of 0.3 m^3 was also constructed. The CO_2 absorption column is designed in such a way that when filled with alkaline solution and purged with exhaust gas from the Hazira plant's vent, CO_2 will be absorbed into the solution. The CO_2 or the vent gas was purged at the bottom of the reactor so as to increase contact time between the gas and the liquid for maximum absorption. The flow rate of the vent gas from te train used was 5.142 litres /minute. Followed by purging, the solution was passed into the high rate pond reactor where algae was grown. Initially the high rate pond was inoculated with Chlorella sp. alone and later we used a consortium of algae i.e *Scenedesmus dimorphus*, *Chlorella vulgaris, Chlorococcum humicola*. The CO_2 sequestered medium was added to algal pond at a flow rate of 45 L/day so as to provide hydraulic retention time of approximately 5 days. The installation pictures as well as experimental set up is shown below.

CO_2 absorption column Algal high rate reactor

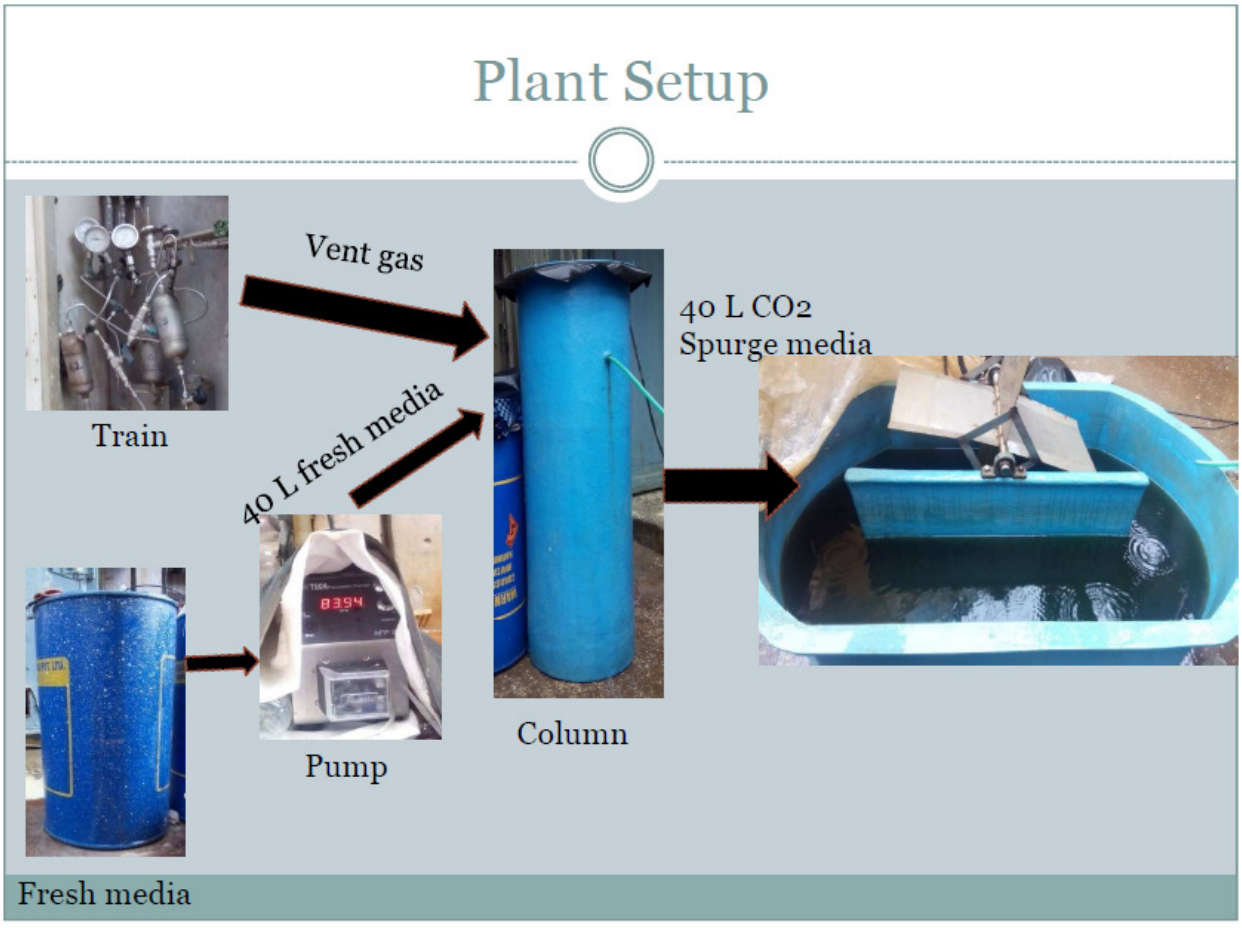


Figure 1: Carbon dioxide sequestration by algae experimental set up.

Screening of microalgae and selection of robust species at lab scale

Phycospectrum (PERC) conducted a screening experiment employing a photobioreactor (PBR) fabricated for CO_2 experiments. A specially designed PBR with a 20 L capacity is connected to an aerator for mixing and an outlet and inlet connected to a carbonation column which works with a motor, non-return valve, regulator and CO_2 meter. The CO_2 pressure was maintained at 0.3 L/min throughout the experiments. The culture was maintained in a semi-continuous mode removing 30 % to a maximum 50% of culture every day to maintain required cell numbers and adding fresh medium. The composition of the growth medium was tap water with 100 mg/L urea and 50 mg/L super phosphate added every time along with trace elements. CO_2 tolerance of various species of selected micro algae was studied by sparging CO_2 and measuring pH every minute using a handheld Eutech pH meter. Time taken for the pH to reach 7 from the initial pH of around 8 was noted for every species. The experiments were repeated by maintaining different levels of cell density (100 to 500 X 10^4/ml). Selected species of micro algae were mixed in to a consortium and growth and pH were monitored. Cell counts were made before and after every time the culture was harvested/diluted for calculating the average growth rate. Based on these experiments a consortium of micro algae ***Chlorella vulgaris***, ***Scenedesmus quadricauda*** and ***Chlorococcum humicola*** which exhibited rapid growth and better tolerance in terms of time taken to reach pH 7, was selected for pilot trials at ONGC's Hazira Plant along with Chlorella sp isolated at BITS Pilani K K Birla Goa campus..

Table 1 Results of preliminary CO_2 tolerance experiments conducted using a 20 L PBR and micro algae cultures from PERC.

Micro algae	**Average Cell density (X10^4 /ml)**	**Growth rate (divisions/day)**	**Time taken for pH to drop from 8 to 7**
Chlorella vulgaris	100	0.66	15
	200	0.68	20
	500	0.70	**25**
Scenedesmus quadricauda	100	0.80	15
	200	0.79	18
	500	0.82	**26**
Desmococcus olivaceous	100	0.61	10
	200	0.56	12
	500	0.52	15
Chlorococcum humicola	100	0.84	15
	200	0.88	20
	500	0.91	**30**

Chroococcus turgidus	100	0.75	10
	200	0.67	12
	500	0.70	14
Oocystis borgei	100	0.45	5
	200	0.52	10
	500	0.46	12
Dactylococcopsis raphioides	100	0.70	10
	200	0.81	12
	500	0.69	12
Consortium of selected micro algae	**200**	**0.87**	**45**

Growth studies of *Chlorella sp.*:

Algal strain *Chlorella* sp. previously isolated at BITS Pilani was checked for its growth on f/2 media at varying pH. The media composition is as follows

f/2 Medium

$NaNO_3$ (75.0 g/L dH_2O)	1.0 ml
$NaH_2PO_4 \cdot H_2O$ (5.0 g/L dH_2O)	1.0 ml
f/2 Trace Metal Solution	1.0 ml
f/2 Vitamin Solution	0.5 ml
Filtered seawater to	1.0 L

f/2 Trace Metal Solution:

$FeCl_3 \cdot 6H_2O$	3.15 g
$Na_2EDTA \cdot 2H_2O$	4.36 g
$CuSO_4 \cdot 5H_2O$ (9.8 g/L dH_2O)	1.0 ml
$Na_2MoO_4 \cdot 2H_2O$ (6.3 g/L dH_2O)	1.0 ml
$ZnSO_4 \cdot 7H_2O$ (22.0 g/L dH_2O)	1.0 ml
$CoCl_2 \cdot 6H_2O$ (10.0 g/L dH_2O)	1.0 ml
$MnCl_2 \cdot 4H_2O$ (180.0 g/L dH_2O)	1.0 ml
Distilled water to	1.0 L

f/2 Vitamin Solution:

Vitamin B_{12} (1.0 g/L dH_2O)	1.0 ml
Biotin (0.1 g/L dH_2O)	10.0 ml
Thiamine HCl	200.0 mg
Distilled water to	1.0 L

As shown in the figure 2 below, the algae could grow at pH from 6 - 10.

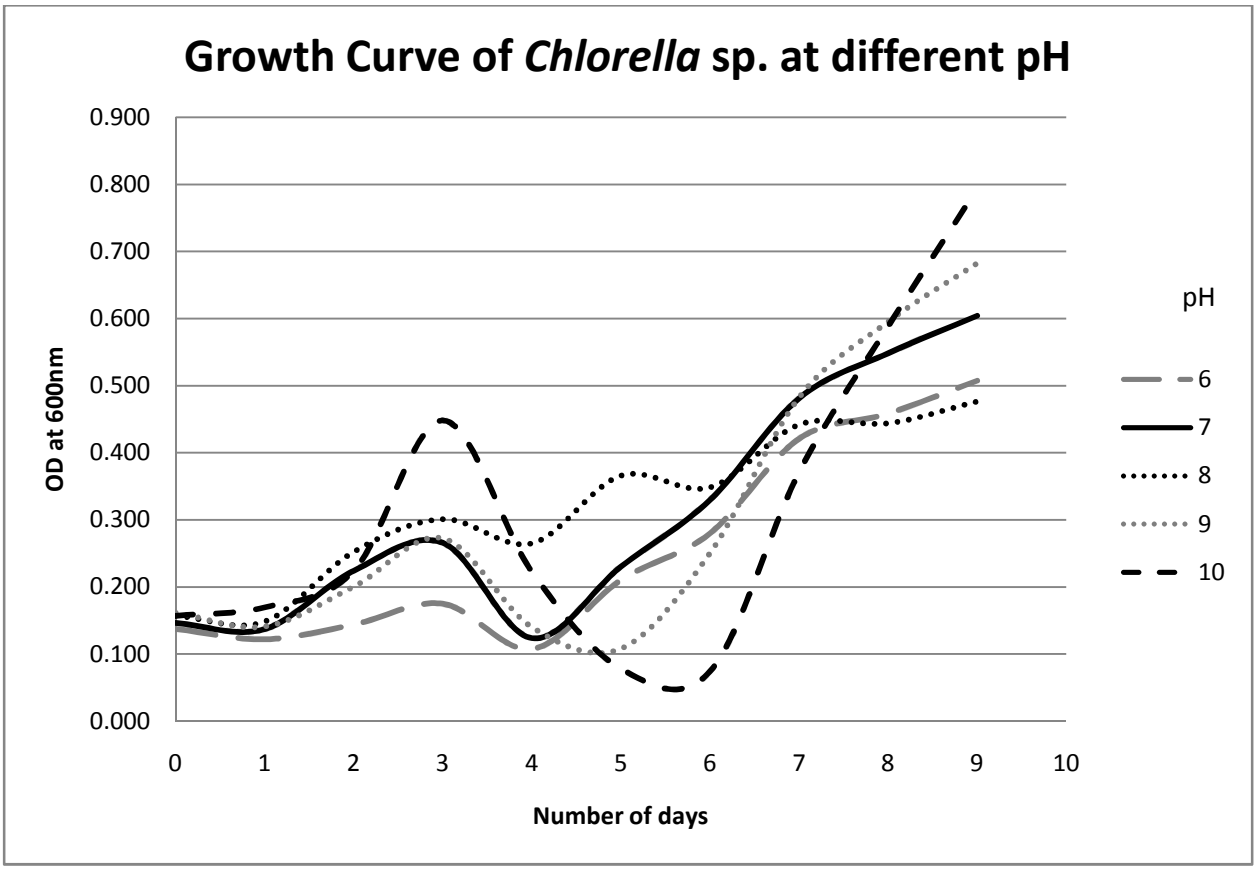


Figure 2 **Growth studies of *Chlorella sp.* (Algal strain from BITS Pilani) at varying pH**

Following the above study, Growth of *Chlorella* sp at pH 7.5 was studied in the presence of air bubbling by aquarium aerator and growth in the presence of vent gas while purging. The growth results are shown below in Figure 2. The *Chlorella sp.* could grow well when purged with vent gas indicating no toxicity of vent gas on the algae selected (Figure 3).

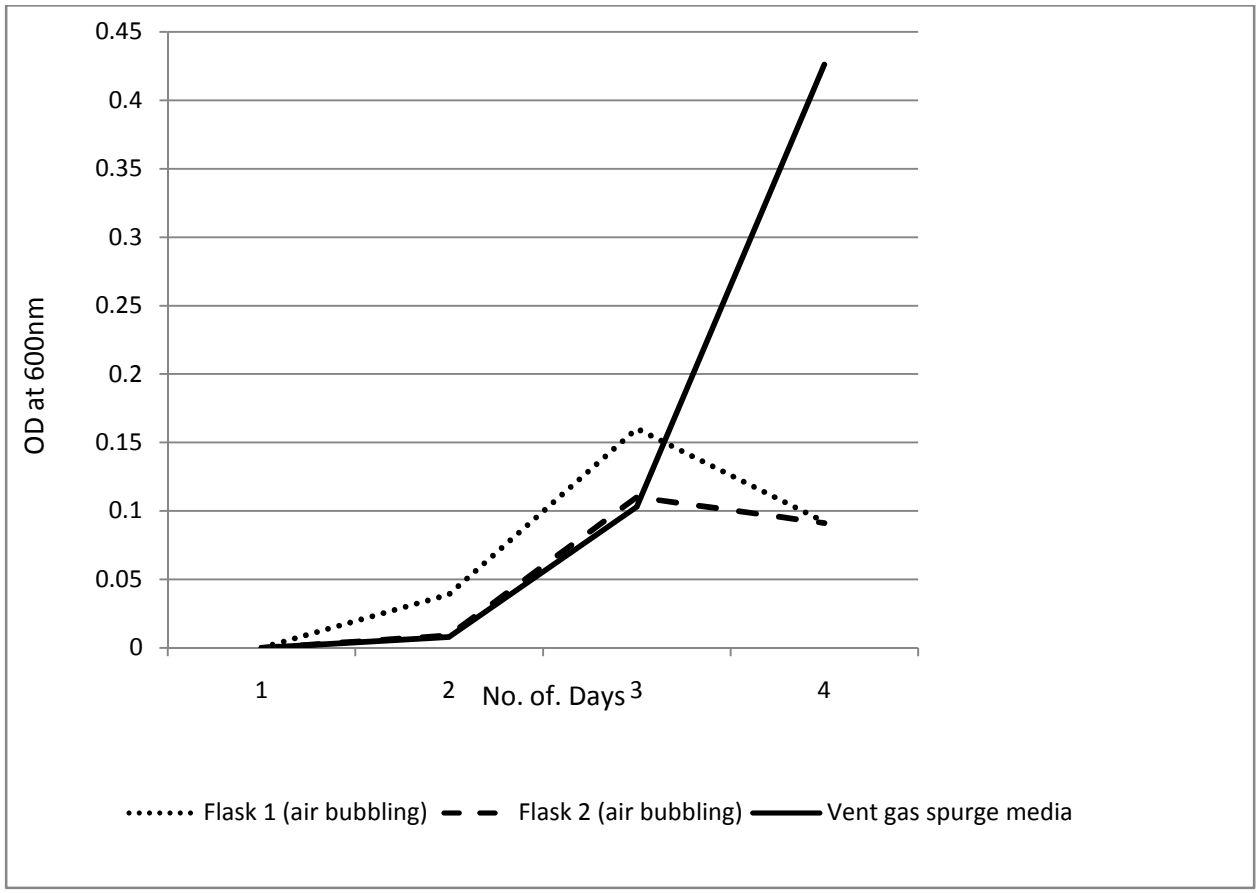


Figure 3 : Algal growth when purged with vent gas

Figure 4: Growth of *Chlorella sp.* When purged with vent gas.

Carbon dioxide sequestration studies:

Photosynthetic algae requires carbon dioxide for its growth and they also can utilize carbon dioxide in the form of soluble carbonates. The following work tested the absorption of carbon dioxide in alkaline algal medium which was later used for algal growth.

Experimental set up and initial results:

The experimental set up is shown in figure 1. The drum of 200L capacity is used to store f/2 medium prepared at pH 11. From the drum, 40L of medium is pumped into the carbon dioxide (CO_2) absorption column per day. The medium in the CO_2 absorption column was continuously purged with the vent gas. The vent gas comes at a pressure of 0.5 bars. The CO_2 absorption column is completely closed so as to collect the outlet gas and analyze so as to quantify the CO_2 absorbed in the medium. The CO_2 absorption column is of 300L capacity with a working volume of 200L. A pilot raceway pond with a volume of 0.2 m^3 is used for growing algae (*Chlorella sp.*), following f/2 medium passing through CO_2 absorption column. The flow rate is 40 L/day and the HRT, 5 days. Everyday 40L of f/2 medium with algal biomass is removed from the raceway pond. The CO_2 concentration in the medium either in column or in the pond was measured by standard titration method. The CO_2 concentration in the vent gas before and after passing it through CO_2 absorption column was measured by Gas

chromatography. The pH and conductivity of the media in the column and in the pond are measured by pH and conductivity meter. The growth of the algae in the pond was monitored by measuring the optical density at 600nm. The results are shown in Table 1.

The growth of the algae increased which is shown in increase in O.D from 0.001 to 0.402. The pH of the medium decreased from pH 11 to around 6.8 – 7.0 in the CO_2 absorption column due to purging of vent gas which contains CO_2. Due to algal growth, the pH in the pond gradually increased to 9.5 – 10. The level of pH rises as a result of CO2 fixation during photosynthesis as OH- accumulates in the growth solution. The yield of *Chlorella sp*. was found to be 18g/m^2/day.

Figure 5: Algal growth in the raceway pond

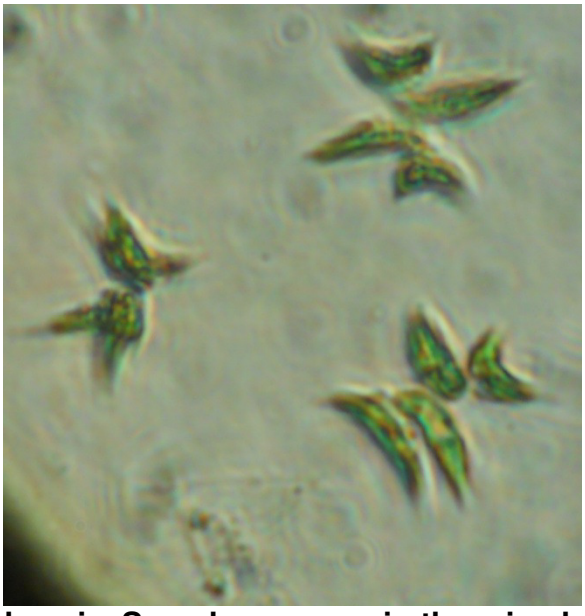


Figure 6: Dominant algae i.e Scendesmus sp. in the mixed algal samples

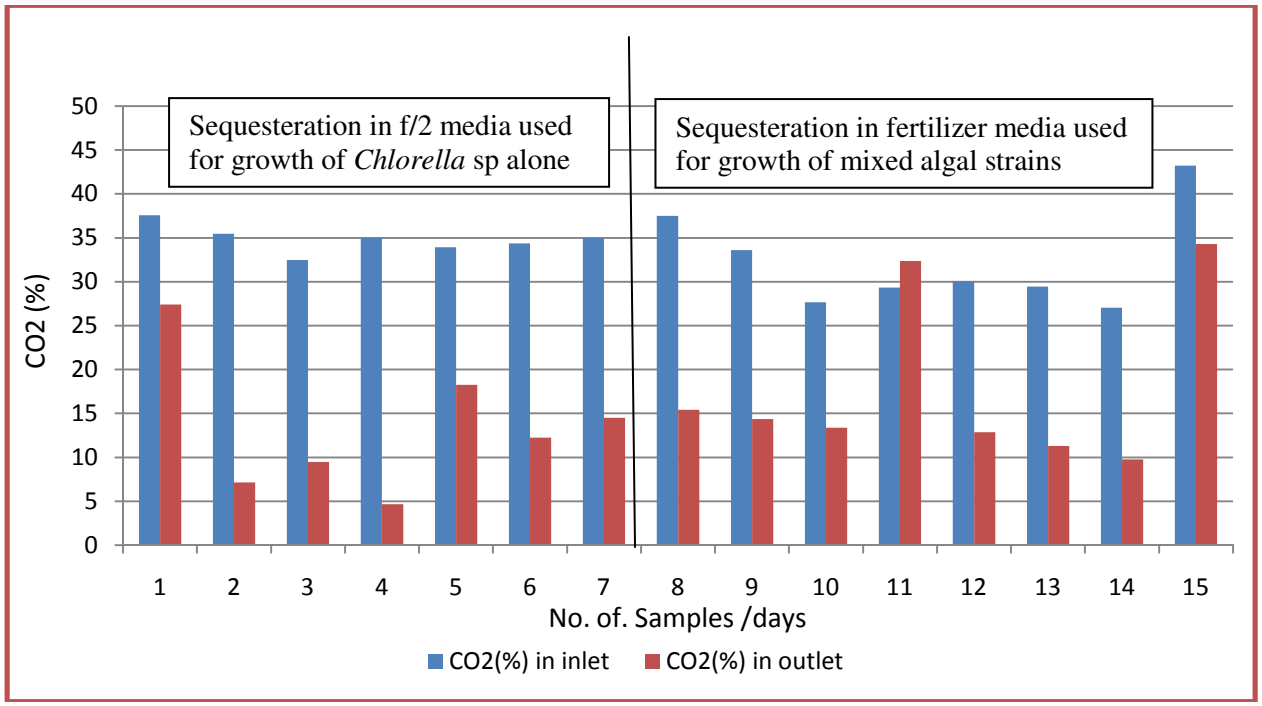


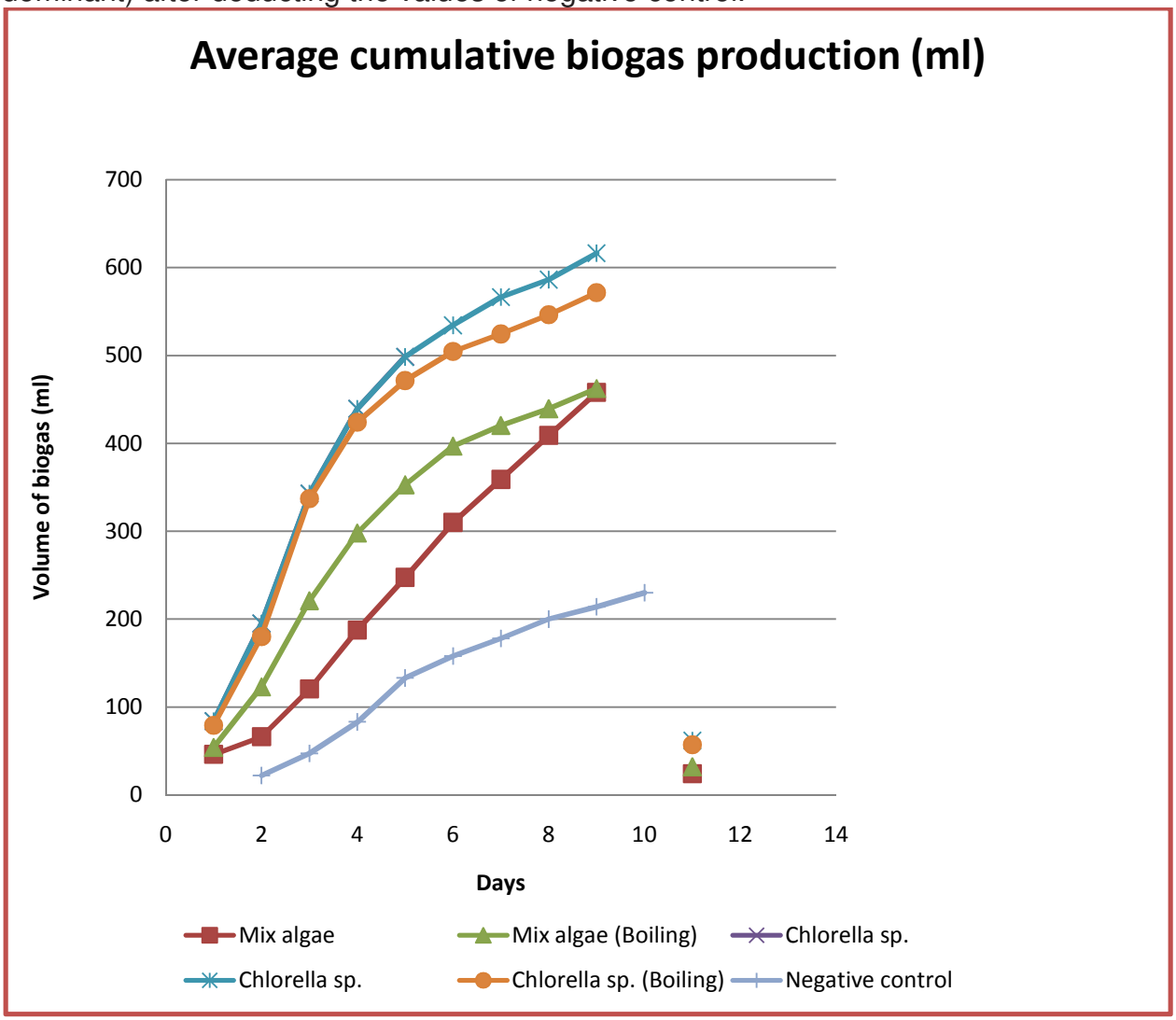
Figure 7: CO_2 absorption studies f/2 media and in fertilizer media.

Anaerobic digestion studies:

The objective of the present study is to assess the bio methane potential of *Chlorella sp.* as well as mixture of algae using Biochemical Methane potential assays. The algae was harvested at site in Hazira during sequesteration studies and sent to BITS Pilani K K Birla Goa campus for anaerobic digestion studies. Sludge from an anaerobic pilot reactor enriched on ethanol was used as inoculum with 40gVS/l. The total Solids (TS), volatile Solids (VS) , COD and total kjeldahl nitrogen were analyzed by standard methods (APHA 1998) before carrying out the anaerobic digestion studies. The VS/TS ratio for algae was found to be 85%. The biochemical methane potential of Chlorella sp. as well as mixture of algae was performed according to Chynoweth and owens (1993); Andelidaki and Sanders (2004) and Angelidaki et al (2009). Experiments were conducted in 600 ml serum bottles in batch mode at 37^{o}C. The reactors were seeded with anaerobic sludge (3g VS/L). The reactors were provided with synthetic growth medium containing nutrients, trace elements and bicarbonate. The headspaces of the reactors were purged with N_2 gas at the beginning of the experiment. The reactors were mixed manually once a day. Biogas production and composition was measured. Gas samples were taken periodically for composition analysis by gas chromatography (Chemito gas chromatography). Methane production is expressed under standard conditions (0^{o}C;1.013x10^{5}Pa).

The anaerobic biodegradability of *Chlorella sp.* as well as mixed algae was evaluated at organic loading rate of 0.5gVS/l/d. The batch digestion results showed that the mixed algae with *Scenedesmus sp.* as the dominant algae in it required longer time to complete the digestion and *Chlorella sp.* has higher biogas yields than mixed algae. The

average methane content of the biogas for *Chlorella sp.* as well as *Scenedesmus sp.* dominated mixed algae was 55%. A pretreatment step of boiling the algae so as to disrupt the cells did not improve the biogas production as evident from the figure.
When the process is operated at low loading rate and high hydraulic retention time, the methane yield (L CH_4/g VS fed) is constant and maximal i.e 386 L CH_4/g VS fed of *Chlorella sp* whereas 228 L CH_4/g VS fed of mixed algae (*Scenedesmus sp.* was dominant) after deducting the values of negative control.



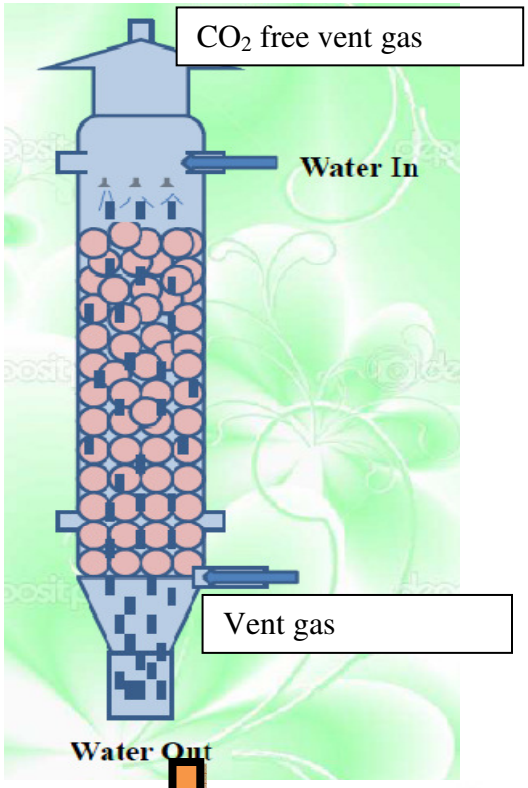
Conclusion:

- The pilot carbonation column is able to bring down 33% initial CO_2 concentration to an average of 15% CO_2 concentration. The whole 33% CO_2 present in vent gas can be sequestered in liquid by employing pressurized water scrubbing

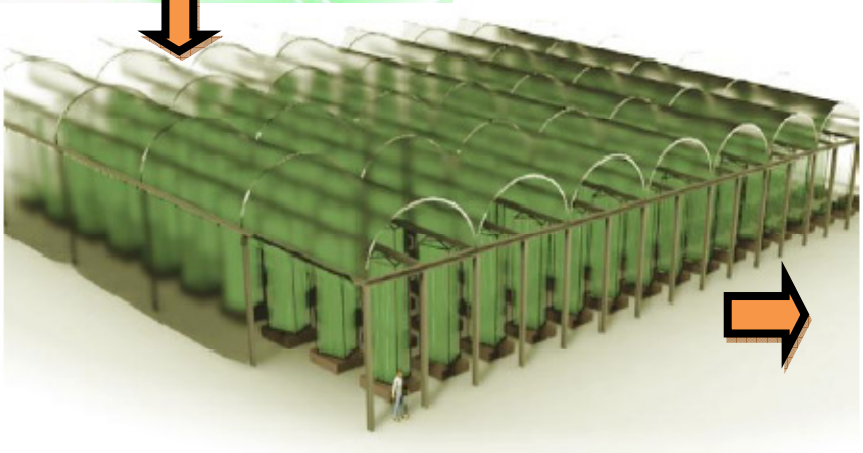
system and the carbonated liquid can be transported to algal ponds / photobioreactors set up. The advantage of the transport of carbonate liquid is its cost effectiveness if land available for the algal growth is limited.

- *Chlorella sp.* yield is about 18g/m^2/day which on anaerobic digestion yields about 386 L CH_4/g VS fed.

Proposed future set up



Counter current water scrubber



Photobioreactor

Anaerobic digestor