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Effect of Water Recirculation Rate on Biogas Upgrading by Algae in Air-lift Photobioreactor

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Abstract

The purpose of this work was to improve the efficiency of carbon dioxide (CO_2) capture from desulfurized biogas by microalgae, i. e. *Chlorella sp.*, in a photobioreactor which comprised an absorption column and an aeration column. The light intensity was controlled at 3,207 lux while the biogas and air flow rates were fixed at 0.045 and 3.600 liters per minute, respectively. The medium recirculation rate between the two columns had a range of 0.25-1.25 liters per minute to study the CO_2 capture performance. The results showed that the CO_2 removal efficiency depended on the recirculation rate and the maximum efficiency was found to be 78.5%. The higher recirculation rate resulted in the higher CO_2 removal rate which could increase the methane content in the biogas to be as high as 25.2% . It was found that 1 kilogram of microalgae could absorb 354 kilogram of CO_2 annually.

Keywords:

biogas upgrading, CO_2 reduction, Chlorella sp., photobioreactor

1. Introduction

Nowadays the consumption of fossil energy is still increasing continuously despite the rapid development of alternative energy. In 1997, anthropogenic sources released 7.4 billion tons of CO_2 into the atmosphere and it is estimated that the number will be up to 26 billion tons by the year 2100. [1] CO_2 is the main cause of global warming and needs to be managed before being released into the atmosphere [2] One of the CO_2 capturing techniques that has drawn attention recently is microalgae cultivation which is able to fix CO_2 and convert it to biomass through the photosynthesis process. Most research works focus on the CO_2 uptake rate and capacity of different alga species [3]. Among them, *Chlorella* sp., a microalgae that can grow rapidly in many media including wastewater, and has been widely used to study CO2 reduction. It was reported that 1 kilogram of dry weight microalgae can absorb CO_2 as high as 1.83 kilograms per year [4].

Biogas, a form of alternative energy, is a product from the anaerobic digestion of agricultural wastes, e.g. livestock manure and agro-industrial wastewater, by methanogenic bacteria. The utilization of biogas can be in a form of heat, electricity or vehicle fuel which help in reducing greenhouse gas emissions into the atmosphere [2]. Raw biogas is a mixture of 40-75% methane, 15-60% carbon dioxide, 0-1% oxygen, 0-2% hydrogen sulfide and almost saturated moisture, depending on the characteristics of the organic matters. Nevertheless, using raw biogas without any purification is very harmful as hydrogen sulfide might cause corrosion to the engine. Too much CO_2 presented in the composition lowers the heating value of biogas and hence decreases the combustion efficiencies [5]. There are several technologies for upgrading biogas such as physical absorption, chemical conversion, membrane separation, pressure swing adsorption and cryogenic separation [6]. However these methods demand high investment costs, consume large amounts of chemicals and energy as well as generate wastes in their processes [7]. The CO_2 capture by microalgae in a photobioreactor is promising as it requires less investment and lower energy consumption than the others. Algae is composed of valuable organic compounds, i.e. carbohydrates, proteins and fats, which can be utilized as food supplements fertilizer and biofuel. There have been a few works related to CO_2 reduction by using microalgae recently. Krit *et al.* (2014) studied the capture of CO_2 by *Chlorella* sp. in 8 liter air-lift photobioreactor by feeding desulfurized biogas at the rate of 0.040 liter per min for 60 minutes and alternately switched to 30 minute of aeration and found that the CO_2 content in the biogas was reduced by 70% and CH_4 content increased from 70% up to 80% by volume [8]. Meier *et al.* (2015) studied the capture of CO_2 by microalgae using two connected photobioreactors in order to operate the biogas upgrading continuously and found that, with the water recirculation rates of 14.4, 41.8, 72.0 and 115.2 liter per day and the biogas flow rate of 7.9 liter per day, the efficiencies of CO_2 removal were 95%, 89%, 80% and 75% respectively [9]. In this work, the study of CO_2 reduction in desulfurized biogas by cultivation of *Chlorella* sp. with poultry wastewater as a growing medium was conducted in order to investigate the effects of liquid recirculation rate between two connected photobioreactors on the biogas upgrading efficiency.

2. Materials and Method

2.1 Microalga

The *Chlorella* sp. used in this study was obtained from the collection of the Department of Biology, Faculty of science, Chiang Mai University.

2.2 Photobioreactor

The photobioreactor was an air-lift type connected to an aeration column made of a clear acrylic cylinder with the height and diameter of 150 cm and 10 cm, respectively. The inner column was smaller with a size of 120 cm in height and 4.5 cm in diameter. The working volume of the reactor was set to be 9 liter. The column was aligned to the center to ensure the uniform exposure of to light which had the intensity of approximately 3207 lux from four 36-W cool white fluorescent lamps. Figure 1 shows the schematic diagram of the photobioreactor.

2.3 Biogas

The biogas used in this study was obtained from an anaerobic digester of a local swine farm. The biogas was desulfurized by using iron sponge reactors in order to limit the H_2S concentration below <100 ppm.

2.4 Methodology

The microalga was cultivated in the reactor at the initial concentration close to 1000 mg/L in a growing media which was a mixture of chicken-manure digester effluent and clean water, containing a total Kjedahl nitrogen (TKN) of approximately 250 mg/L [10]. The properties of the effluent are shown in Table 1. The microalgae concentration was measured by the gravimetric method (APHA 1985) and an OD meter at 665 nm wavelength (JENWAY). The air-lift photobioreactor was connected to the aeration column operated in counter flow mode. Each unit of the reactor contained 9 liters of culture microalgae. Microalgae culture was continuously circulated between the photobioreactor and the aeration column by means of a peristaltic pump. The system was operated by injecting biogas into the bottom of the photobioreactor at the rate of 0.005 vvm (reactor volume per minute) or equivalent to 0.045 lpm [8]. In the aeration column, the culture was aerated at 0.4 vvm or 3.6 lpm. Five liquid recirculation flows between aeration column and photobioreactor were studied: 0.25, 0.50, 0.75, 1.00 and 1.25 lpm, equivalent to the liquid-to-gas ratio (L/G ratio) of 5.56, 11.11, 16.67, 22.22 and 27.78, respectively. Liquid samples were periodically taken from the column to determine pH (EZDO model 6011). Gas samples were taken from sampling ports located at the entrance and exit of the photobioreactor for the determination of gas composition (Geotechnical Instrument, Biogas check). The CO_2 removal and CH_4 enrichment efficiencies were then determined using the following formulas:

$$CO_2 \text{ reduction } (\%) = \frac{(C_{CO2}\text{ inf} - C_{CO2}\text{ eff})}{C_{CO2}\text{ inf}} \times 100\% \quad (1)$$

$$CH_4 \text{ enrichment } (\%) = \frac{(C_{CH4}\text{ eff} - C_{CH4}\text{ inf})}{C_{CH4}\text{ inf}} \times 100\% \quad (2)$$

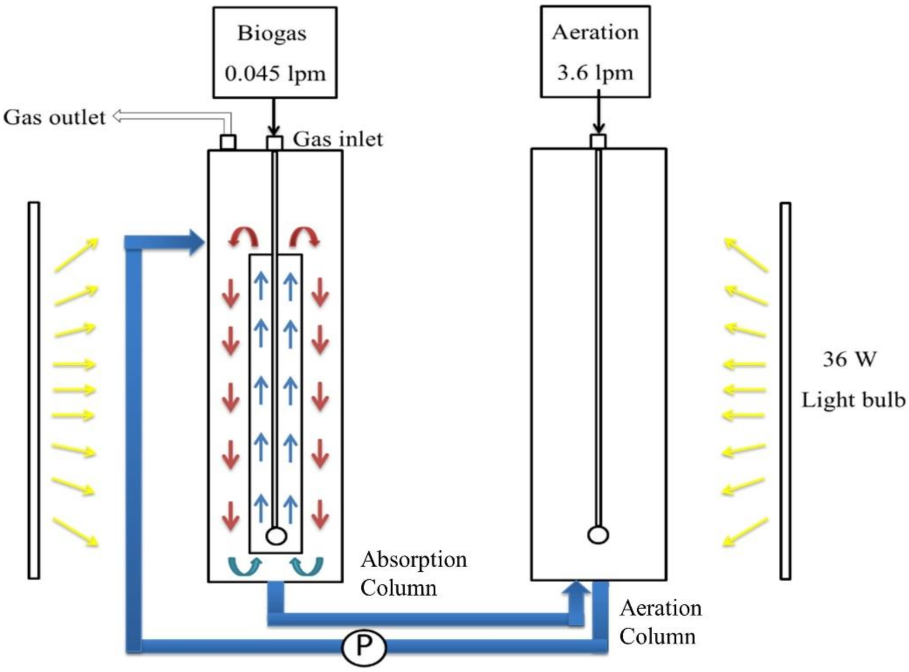

Fig. 1 Schematic diagram of the photobioreactors and their liquid flow directions.

3. Results and Discussion

3.1 The growth rate of Chlorella sp.

Table 1 Characteristic of effluent of poultry wastewater extract.

Parameter	mg/l
COD	2116.8
TKN	1136.8
SS	273.2
VSS	232.0
pH	8.1

Each experiment was conducted with the initial concentrations of *Chlorella* sp. at approximately 0.75 g/L and the system was operated with the liquid recirculation rate of 0.25 to 1.25 lpm. It can be seen in Figure 2 that at higher liquid recirculation rates, the algae concentration was higher because the algae could uptake more carbon dioxide and convert it to biomass. The algae concentrations of any recirculation rate increased rapidly within the first two days and levelled off after that since there was excessive dissolved carbon dioxide that changed the pH of the media. Also, the limited nutrients in the media could hinder the algae growth rate during longer times [11].

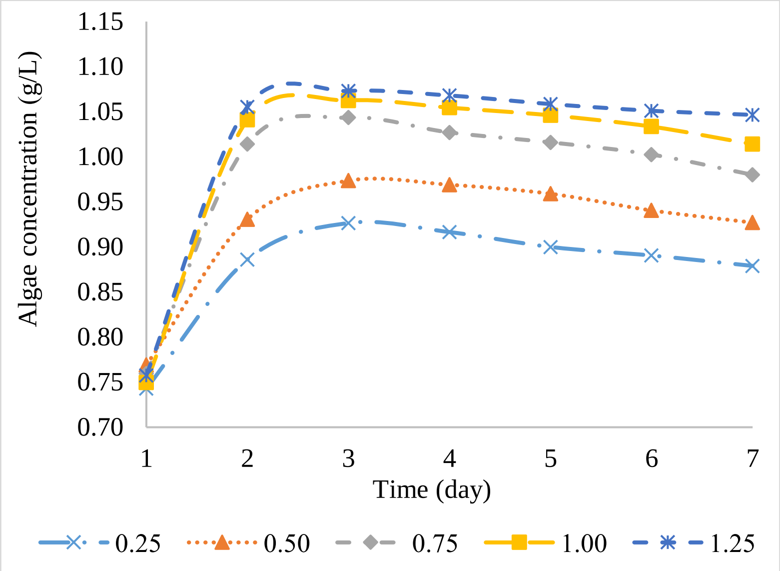

Fig. 2 Concentration of *Chlorella* sp. in the 7- day at the recirculating rate of 0.25 – 1.25 lpm.

3.2 Efficiency of CO_2 reduction and CH_4 enrichment

3.2.1 Reduction of carbon dioxide in biogas

In each experiment, the biogas was fed into the photobioreactor continuously to promote the growth of the algae that absorbed carbon dioxide. The biogas composition entering and exiting the reactor was measured hourly. The initial CO_2 concentration was in a range of 25.8 to 29.0% by volume and the exit CO_2 concentration varied depending on the liquid recirculation rates. The CO_2 absorption occurred at a very high rate at the beginning. For instance, the CO_2 content was reduced as low as 6.2% by volume in the first 30 minutes of the experiment with the recirculation rate of 1.25 lpm. The CO_2 removal gradually decreased when the liquid become more saturated with the gas. Figure 3 illustrates the average 7-day concentration of CO_2 in the biogas after passing through the column. As can be seen the concentrations were reduced from the initial concentrations to less than 17.2 % by volume. The reduction of CO_2 occurred due to the combination of photosynthesis by the algae and its inherent water solubility. It can also be seen that the CO_2 concentrations in the experiments with algae were lower than those without algae by 17.4-30.8 percent.

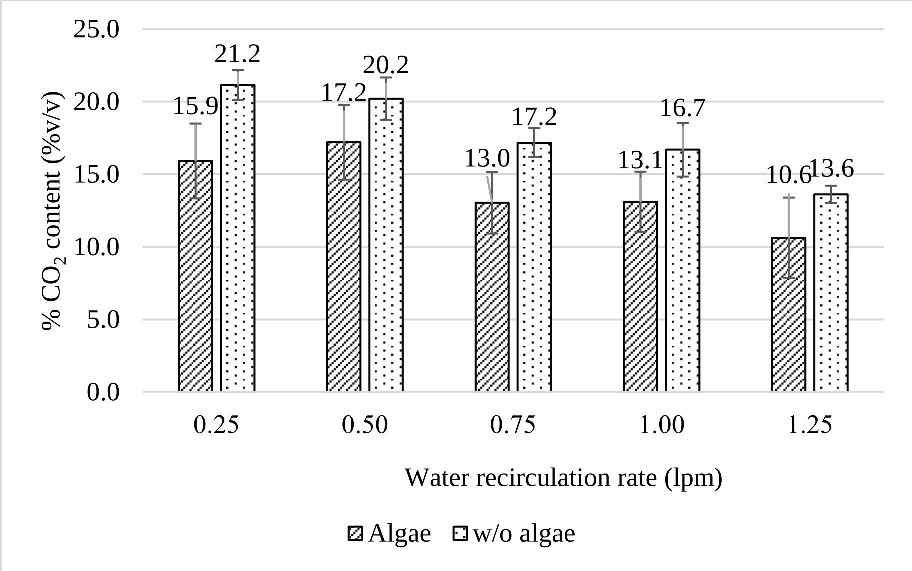

Fig. 3 The CO_2 content of the exiting biogas from the photobioreactors with and without *Chlorella* sp.

Fig. 4 shows the efficiency of CO_2 reduction at different liquid recirculation rates. In general, the higher CO_2 reduction was associated with the higher recirculation rate because the algae came in contact with more CO_2. Also, the physical absorption and desorption of CO_2 in the absorption column and the aeration column occurred at a higher rate when the liquid recirculation was high. The maximum average CO_2 removal efficiency was 63.1 percent, comparable to the previous work which studied the non-recirculation experiment and found that the absorption column could remove CO2 content by 72.27% [8]. Keffer et al. (2002) cultivated *Chlorella vulgaris* in the photobioreactor with a working volume of 1,500 liter. After 12 seconds of the experiment, CO_2 was reduced up to 76% from the influent air with the initial CO_2 concentration of 0.16% by volume [12]. The similar result show that CO_2 reduction decreased over time.

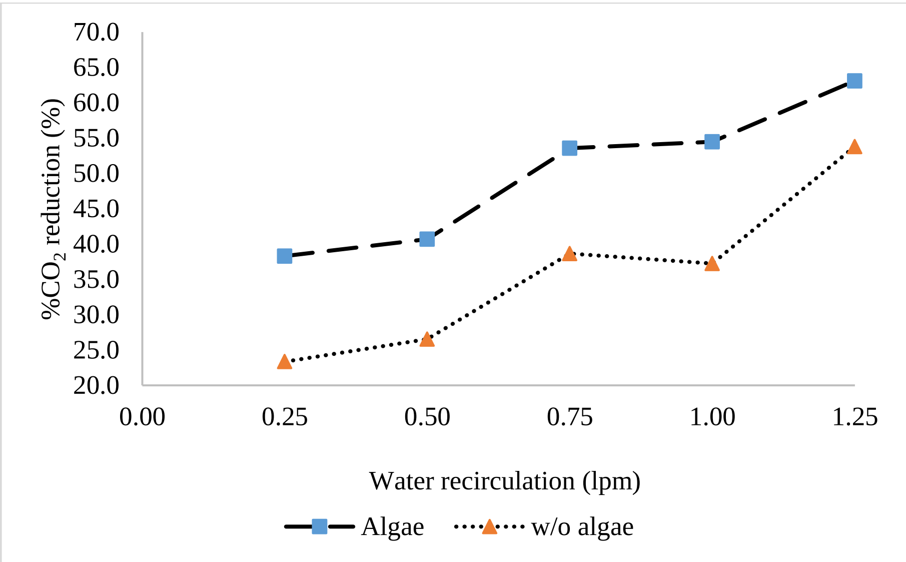

Fig. 4 The CO_2 reduction by the photobioreactors with and without *Chlorella* sp.

The specific CO_2 absorption per mass of algae was calculated by comparing the experiments with and without algae in order to take out the effect of physical absorption. The results are shown in Figure 5. As can be seen, the specific CO2 absorption per mass of algae in the first day were in a range of 9.5-14.0 gram of CO_2 per gram of dry algae and remained in the same range for 5 days. Some decreases were observed at the latter days as expected due to the combined results of changing pH, algae aging and limited nutrients which affected the growth rate of the algae. It can be noticed that the specific CO2 absorption per mass of algae at a high recirculation flow rate (1.25 lpm) decreased drastically over time. There was no certain reason for this but it is expected to be the result of a vigorous flow regime which deteriorated the condition for algae growth.

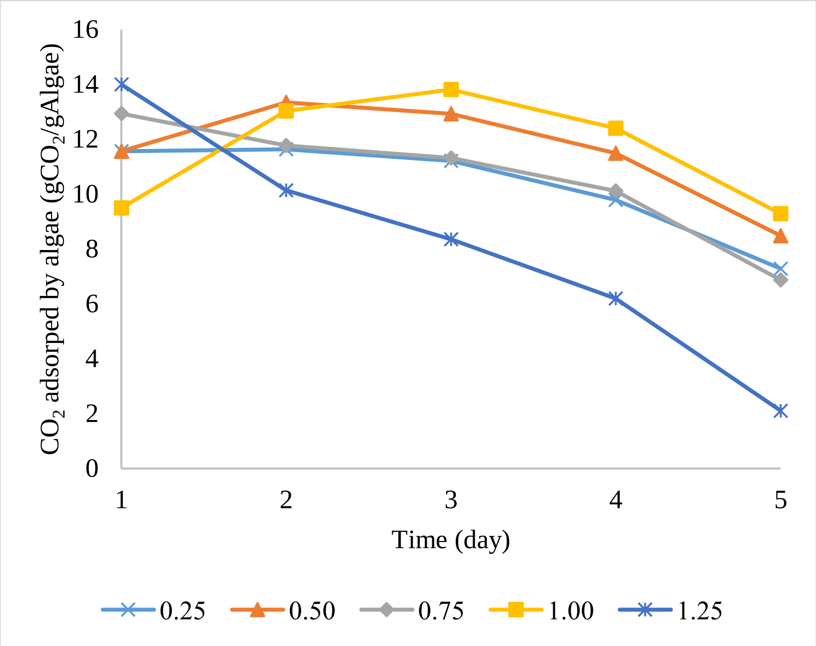

Fig. 5 The specific CO_2 absorption per mass of algae at different recirculating flow rates.

3.2.2 Methane enrichment of Biogas

When the CO_2 in biogas was absorbed and consumed by algae, the methane content was proportionally increased. Figure 6 illustrates the average 7-day methane content of the exiting biogas at different recirculation flow rates. The initial methane concentration was in a range of 65.9-68.2% by volume and the exit methane concentration varied depending on the liquid recirculation rates. As can be seen the methane could be enriched from the initial concentrations to as high as 76.8% by volume. Kao et al. (2012) studied mutant microalgae which could tolerate high levels of CO_2 and found that the methane could be enriched from 70% to 85-90% by volume at the biogas flow rate of 0.05 vvm [13]. The methane concentrations in the experiments with algae were higher than those without algae by 1.5-7.3% by volume.

The percentages of methane enrichment by *Chlorella* sp. are presented in Fig. 7. It can be seen that the enrichment efficiencies by algae linearly increased with the liquid recirculation rate and were in a range of 3.9 – 16.6 percent. Such enrichment efficiencies were clearly higher than those of the system without algae by 70.6-160.0 percent at the same liquid circulation flow rate.

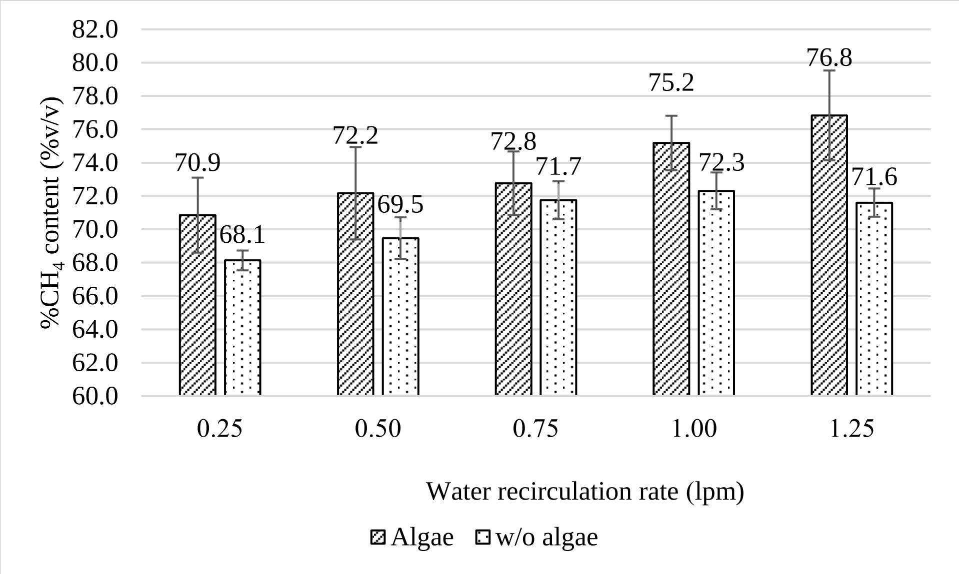

Fig. 6 The CH_4 content of the exiting biogas from the photobioreactors with and without *Chlorella* sp.

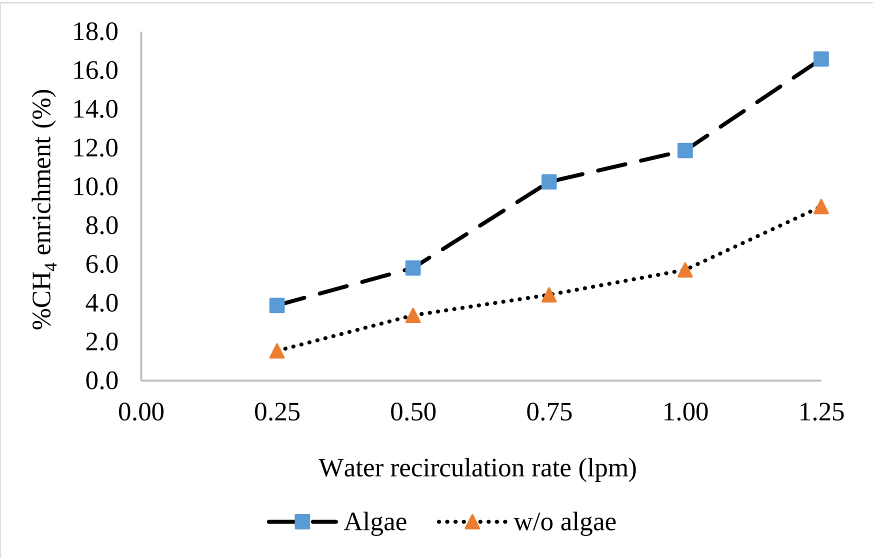

Fig. 7 The methane enrichment of the biogas in the system with and without *Chlorella* sp.

3.3 Variation of pH

The pH values of wastewater with and without *Chlorella* sp. were 7.0 and 7.8, respectively. It can be seen in Figure 8 the pH values decreased over time due to the accumulation of carbon dioxide in the liquid. When biogas was fed into the absorption column, a part of the gaseous carbon dioxide was dissolved and dissociated to different carbonic forms, i.e. $H_2CO_{3(aq)}$, HCO_3^- and CO_3^{2-}, and caused changes in pH of the aqueous solution. These forms could be removed by the uptake mechanism of growing algae and the desorption mechanism in the aeration column. The continuous decrease of pH over time indicated the accumulation of dissolved carbon dioxide in the liquid since the two removal mechanisms could not remove all of the influx of dissolved CO_2. Too low pH could affect the algae growth rate so it is necessary to limit the biogas feeding into the photobioreactor [14]. It can be also seen that at higher liquid recirculation rates, the pH value decreased slowly since the dissolved CO_2 was transferred to the aeration column and stripped off faster.

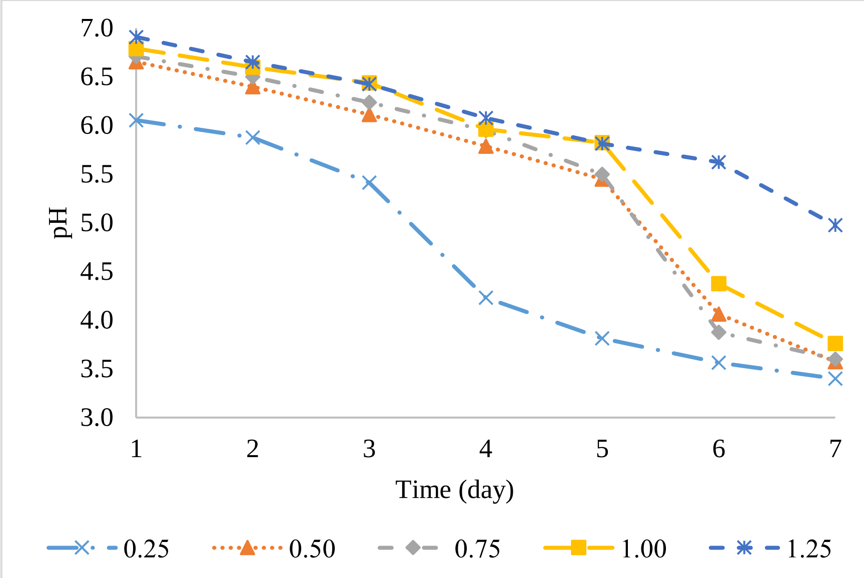

Fig. 8 the pH values of liquid in the system with *Chlorella* sp.

4. Conclusion

The capture of carbon dioxide in biogas using *Chlorella* sp. In an air-lift photobioreactor showed that the system could enrich the methane content by 16.6% and could remove the undesirable carbon dioxide by 63.1%. The liquid recirculation rate was found to be the main factor influencing the overall performance of methane enrichment. The photobioreactor could continuously improve the biogas quality, especially when the recirculation rate was high, and could be applied to many uses, e.g. Nevertheless, the accumulation of dissolved carbon dioxide and a pH change were negative factors to the system's performance. Therefore there might be studies that focus on the biogas loading rate of the system and continuous addition of nutrients in order to maintain the growth of algae and system performance.

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