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DESULFURIZATION IN A PLATE-TYPE GAS-LIFT PHOTOBIOREACTOR USING LIGHT EMITTING DIODES

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Abstract – Hydrogen sulfide gas was removed in a 2-dimensional gas-lift reactor by the photosynthetic microorganism *Chlorobium thiosulfatophilum* using light emitting diodes (LEDs) as a light source. LEDs saved light energy by 99% compared with the incandescent light source. The plate-type gas-lift reactor removed hydrogen sulfide five times better per unit mg of protein, and performed two times better in the maximum performance per unit luminous flux, compared with cylindrical fermentors.

Key words: *Photosynthetic, Desulfurization, Light Energy, LED, Plate-type Reactor*

INTRODUCTION

The release of hydrogen sulfide gas generated by industrial processes such as desulfurization of natural gas or crude oil refining, and steel or viscous-rayon manufacturing is strictly regulated. High capital and operating costs of conventional physico-chemical treatments of hydrogen sulfide makes biological oxidation of hydrogen sulfide a considerable alternative.

The use of *C. thiosulfatophilum* cells is advantageous for biological sulfide removal because of relatively simple nutrient requirements, no needs of oxygen flow rate control [Buisman et al., 1990; Sublette et al., 1987] and sterilization. Hydrogen sulfide can be converted to elementary sulfur or sulfate by the photosynthetic bacterium *C. thiosulfatophilum* as follows [Cork et al., 1983],

$$2H_2S + CO_2 \xrightarrow{hv} 2\,S^0 + (CH_2O) + H_2O \quad (1)$$

$$H_2S + 2CO_2 + 2H_2O \xrightarrow{hv} 2(CH_2O) + H_2SO_4 \quad (2)$$

where S^0 and $(CH_2O)_n$ indicate elementary sulfur and general formula of carbohydrates produced. The production of sulfur or sulfate results from the electron requirement in the photosynthetic reaction center P840 of the cell chlorophyll. With more light energy sulfate production [Eq. (2)] is favored.

However, this process requires a light energy. Effective and economical supply of light energy is a key factor that determines the success of *C. thiosulfatophilum* application to industrial scale sulfide treatment. Kim et al. [1991a] used LEDs to supply the specific wavelength of light at which *C. thiosulfatophilum* absorbs selectively, and saved 95% of the light energy as compared with the incandescent bulb. The bacteriochlorophyll of *C. thiosulfatophilum* absorbs 460- and 760-nm light and the carotenoid pigments absorb supplement light other than those absorbed by the chlorophyll. An incandescent bulb has a broad wavelength spectrum from 400 nm but emits most of its light energy beyond 850 nm as heat. The LEDs having a narrow bandwidth from 600 to 800 nm can increase the efficiency of light energy utilization significantly.

In the previous work [Kim et al., 1992] the removal rates of hydrogen sulfide per unit mg of protein in the 4-L conventional cylindrical fermentor was smaller than that in the 2-L fermentor. This decrease of performance per unit mg of protein could be explained by the higher light attenuation in the larger reactor. With the progress of the reaction the concentration of the cell and sulfur particle and the turbidity of the system increase. This results in a poor penetration of light into the reactor. Inside the reactor some dark zone is formed where the light does not reach. If the reactor is bigger, the ratio of light penetration depth to its radius becomes smaller. Poor illumination can results in a decrease in performance. It is important to design a reactor which can utilize the available light energy adequately. Ideally, the reactor should have a large surface area to transmit the light. In order to get a higher surface area to volume, we applied a 2-dimensional gas-lift reactor. Sulfide removal rates and performance per unit luminous flux for both incandescent light and LEDs were investigated for this plate-type reactor and the previous cylindrical reactor.

MATERIALS AND METHODS

1. Organism and Medium

Chlorobium limicola forma *thiosulfatophilum* (ATCC 17092) was used. The medium in the fed-batch reactor consisted of KH_2PO_4 (0.74 g/L), NH_4Cl (0.74 g/L), $MgSO_4 \cdot 7H_2O$ (1.8 g/L), $CaCl_2 \cdot 2H_2O$ (0.05 g/L), NaCl (7.4 g/L), Vitamin B_{12} (0.0002 g/L) and trace elements with 0.05M phosphate buffer. The feed gas mixture consisted of H_2S (4.16 mol %), CO_2 (9.34 mol %),

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N_2 (86.01 mol %), and H_2 (0.49 mol %) equivalent to 46,385 ppm of H_2S.

2. Reactor System and Operation

We used a 2-dimensional, plate-type, gas-lift reactor with a 30 cm length, 10 cm width, 50 cm height, and a working volume of 11.9 L. On the bottom of the two end sections, sintered glasses (10 cm dia., pore size 1-4 μm, Japan) were attached as spargers, so the two end sections became risers and the middle section became a downcomer. A prism on the bottom of the downcomer section helps the flow disperse easily to the two end sections (Fig. 1).

Feed gas was supplied to the reactor through a gas flow controller and a two stage gas regulator from a standard gas cylinder. But the feed gas flow rate was not high enough to give proper circulation to the media. Additional N_2 gas was used for efficient mixing, and its flow rate was also controlled by a gas flow controller and a two stage gas regulator. The pH and temperature were maintained at 6.85 and 30°C, respectively.

Two sets of zinc acetate in an effluent line were used to scrub hydrogen sulfide gas which was not absorbed in the water. The schematic diagram of the reactor system is shown in Fig. 2.

3. Light Sources

3-1. Incandescent Bulb

Two 100 W incandescent light bulbs were placed to front and rear walls, respectively. Light intensity was determined with a lux meter (IM-2D, Topcon Co., Tokyo, Japan).

3-2. LED (Light Emitting Diode)

LED 710 with a colored clear lens (10 mcd, ULP-R60C-51, U-Jin Co., Seoul, Korea) which has a maximum peak at 710 nm and emits 60% of peak intensity at 760 nm for the chlorophyll was connected to a 330 resistor in series to make the light intensity of each LED uniform. Twenty two sets of such a LED-resistor were connected in parallel. This constituted one row of the LED light source panel. Each panel was made up of 16 such rows which resulted in 352 LEDs per light panel (Fig. 3). Two light panels were placed, one on each face to supply

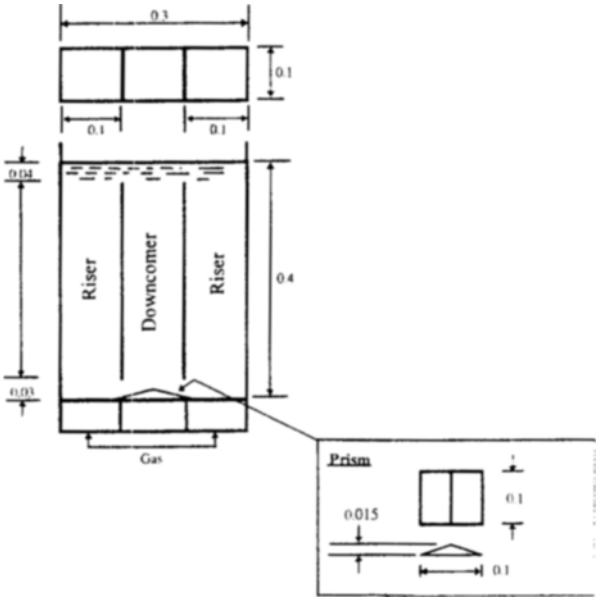

Fig. 1. Configuration of the plate type gas-lift reactor.

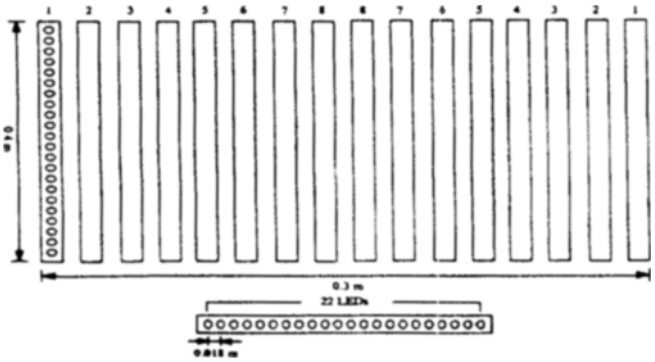

Fig. 3. Array of 16×22 light emitting diodes (LEDs) attached on one wall of the plate-type reactor.

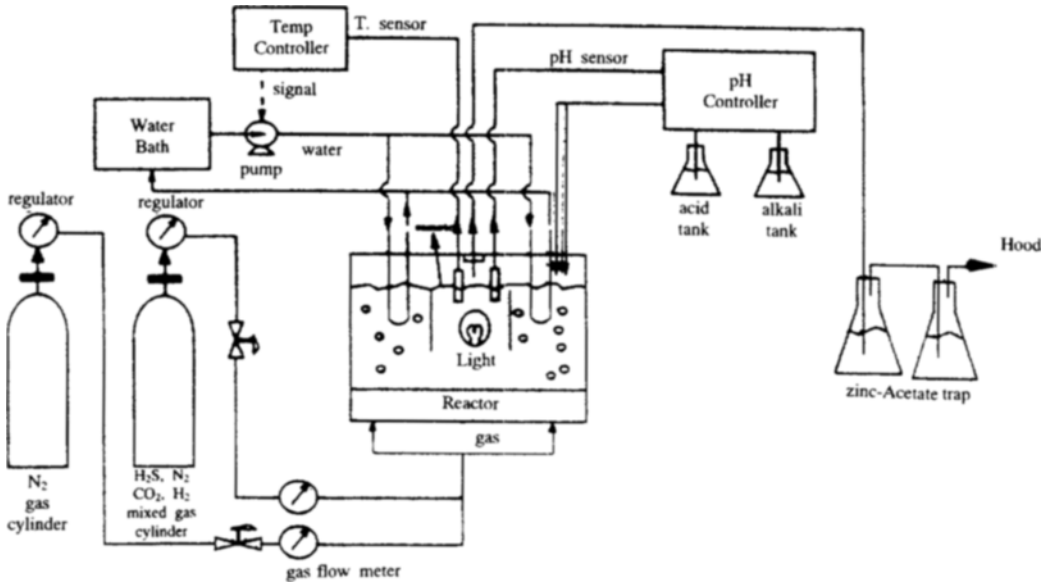

Fig. 2. Schematic diagram of the plate-type gas-lift reactor.

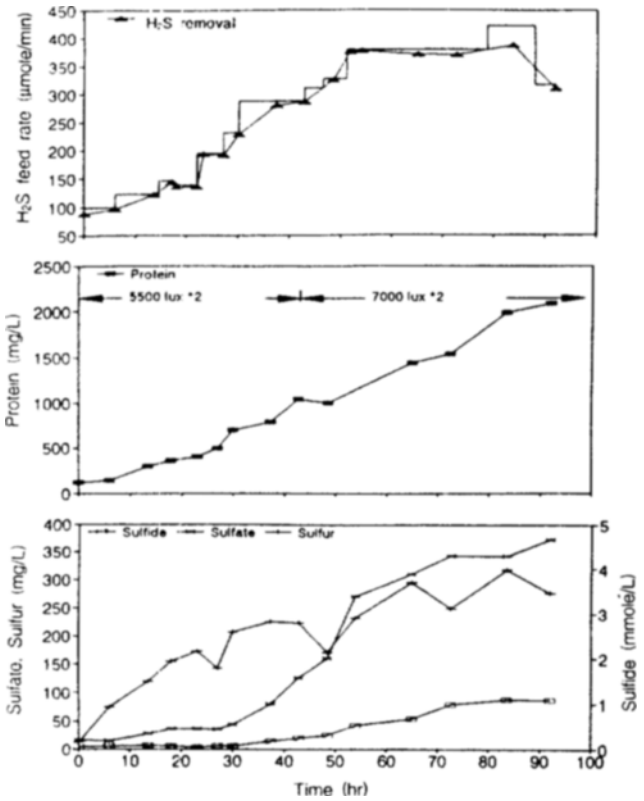

Fig. 4(a). Time courses of H_2S oxidation by *C. thiosulfatophilum* with the flow rate of the additional N_2 gas at 0.7 L/min. Incandescent lights were used as the light source.

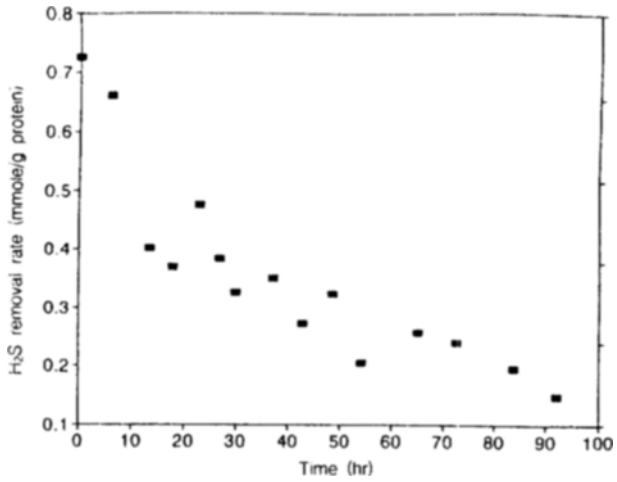

Fig. 4(b). A profile of H_2S removal rate per unit g protein.

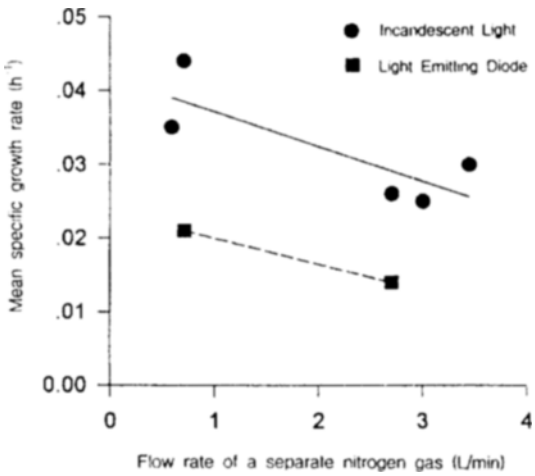

Fig. 5. Mean specific growth rate (h^{-1}) with flow rate of nitrogen gas (L/min).

the reactor with its necessary light energy. In total 6.6 W of power was consumed.

4. Analysis

Sulfide and sulfate were determined by the method described by Greenberg et al. [1981]. Elemental sulfur and cells were precipitated by centrifugation at 18,000 g and 4°C. Sulfur concentration was analyzed by Koch [1949], and cell concentration was not determined directly because of sulfur particles. Knowing that 24% of the dry cell weight is due to protein, we can measure protein concentration by Bradford's method [1976], and thus indirectly measure cell concentration.

Light spectrum was analyzed with a monochromator (Model 2062, McPherson Co., Massachusetts, U.S.A.) where a photocathode (Model 552S, Hammamatzu Co., Japan) was used.

RESULTS AND DISCUSSION

1. Desulfurization with an Incandescent Light Source in a Plate-type Reactor

The flow rate of feed gas mixture expected by H_2S removal per unit mg of cell is not strong enough to mix the media properly, so we used additional N_2 gas as we mentioned earlier. Since the flow rate of this additional N_2 gas was much greater than that of feed gas mixture, it works like carrier gas. Thus the residence time of the gas mixture in the reactor was determined by the flow rate of the additional N_2 gas. If the flow rate of additional N_2 gas is too high, the contact time of gas with the media is too short and H_2S gas does not have enough time to be absorbed by the media. In this case most of H_2S gas escapes from the reactor. With low or no N_2 gas flow rates, sulfur particles precipitate and even deposit on the wall of the reactor. This results in obstructing the light penetration. Even at a high flow rate after certain operation times, sulfur particles were deposited on the wall of the downcomer section. Thus there exists an optimum flow rate. We varied the flow rate of the additional N_2 gas (data are not shown) and determined that a 0.7 L/min of the additional N_2 gas was the optimum flow rate for our system.

Fig. 4 shows a typical run of the experiment. In the beginning H_2S removal rate was low because of low cell concentration. As the reaction progressed further in 40 h, sulfide was accumulated a little in the media. This decrease of the H_2S removal rate was due to the increase of turbidity. After increasing the light intensity from 5,500 to 7,000 lux at 40 h of the experiment, the concentration of sulfate increased considerably. If there is too much light energy available to the microorganisms, CO_2 fixation and microbial growth rate are stimulated,

thus creating a demand for more electrons from any available species of sulfur with oxidation state less than +6. In the final period H_2S removal rate does not increase further due to accumulation of toxic byproducts.

Sulfur concentration did not increase greatly like in the cylindrical fermentor, but actual sulfur production would be greater than those in the figure since many sulfur particles produced used to deposit on the wall of the downcomer section. Furthermore, the top of the reactor was covered with a slurry of cells and sulfur particles. It is because that sulfur particles as well as some part of cells were pushed up and dried in the upper region of the wall.

To prevent the deposit of sulfur particles on the wall, a recycle stream with a sulfur settler can be considered. Kim et al. [1991 b] removed 80% of sulfur particles by using an external sulfur settler. This improved the light transmission to the reactor, and resulted in a 50% increase of the H_2S removal rate. It is predicted that the gas-lift reactor with an external sulfur settler can enhance the performance of the reactor.

Maximum specific growth rates in the conventional cylindrical fermenter were 0.02 to 0.13 h^{-1} depending on the feed rate and light intensity. In the plate-type reactor the specific growth rate tended to increase due to more efficient light irradiation to the wall, which ranged from 0.038 to 0.13 h^{-1} with respect to the variation of flow rate of the separately blown nitrogen gas from 0.58 to 3.0 L/min (Fig. 5). A typical specific growth rate was 0.112 h^{-1} for the flow rate of 0.7 L/min.

2. H_2S Removal Rates in Cylindrical and Plate-type Reactors with an Incandescent Light Source

If the irradiation of light is uniform as possible onto a reactor, the reactor performance will improve. Surface-to-volume ratios were compared for every reactor geometry used in these experiments. If this ratio increases for the same volume and geometry, the illumination effect will increase. The conventional reactors usually have approximately the same geometric ratio of height-to-diameter for a cylindrical fermentor [Wang et al., 1979]. Cylindrical fermentors of 2 L and 4 L in these experiments had nearly the same geometry of 1:1, but the surface-to-volume ratio decreased from 0.303 to 0.235 (Table 1). If the same geometrical ratio is applied to a potential fermentor of 11.9 L same as the volume of plate-type reactor used in this study, the S/V ratio decreases much less to 0.161. The larger volume makes the less S/V ratio; which results in the worse illumination effect. Real effectiveness of illumination decreases more than decrease rate of S/V ratio, since light used to be supplied to each half annular area by each lamp, not fully uniformly in a radial direction.

Plate-type reactor has 24% better S/V ratio than that for a potential cylindrical fermentor with the same volume of 11.9 L. The average light intensity which is integrated over the target area of the wall surface [Cornet et al., 1994] is much better than that for the cylindrical reactor, since the incident light angle in plate-type reactor is nearly normal to the reactor wall. In the following experiment using light emitting diode arrays attached directly onto the wall surface, the average light intensity would increase much better than a pair of incandescent light bulbs in both opposite sides.

These comparisons are summarized with some performance results in Table 1. The maximum H_2S removal rate averaged about 0.136 mmol·L/min·g protein in the cylindrical fermentor with an incandescent light source [Kim et al., 1991]. Even though a direct comparison for the performance is difficult with a cylindrical fermentor of the same volume, the plate-type gas-lift reactor has about five times as that of the 4-L cylindrical fermentor.

3. H_2S Removal Rates in Both Type Reactors with LED's

Table 1. Surface to volume ratios and performance rates with an incandescent light source in photosynthetic desul-

Reactor type	Geometry (cm)	Volume (V; cm^3)	Wall surface (S; cm^2)	S/V (cm^{-1})	Performance (μmol/min)/ (mg-protein/L)
Cylindrical	ID 13.2, H14.6	2,000	605.4	0.303	0.107
	ID 17.0, H17.6	4,000	940.0	0.235	0.136
	ID 24.7, H24.7[1)]	11,900	1,916.7	0.161	-
Plate-type	H39.5, L30.0, W10.0	11,900	2,370.0	0.199	0.662[2)]

[1)]In order to get the S/V ratio for a conventional cylindrical fermentor with the same volume as the plate-type reactor, diameter to height ratio was assumed as 1:1 in a potential cylindrical 11.9-L reactor not used in this study.

[2)]At the separate nitrogen flow rate of 0.7 L/min with the same incandescent light bulbs as cylindrical reactor's

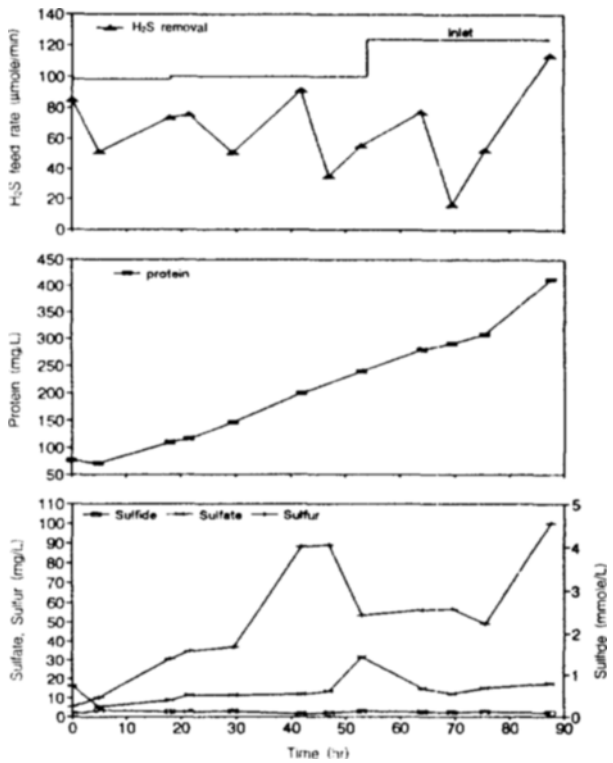

Fig. 6. Time courses of H_2S oxidation by *C. thiosulfatophilum* with the flow rate of the additional N_2 gas at 0.7 L/min. LEDs were used as the light source.

Table 2. Summary of averaged maximum specific growth rate, H_2S removal rate, and performance of H_2S removal per unit luminous flux

	Maximum specific growth rate (h^{-1})	Maximum H_2S removal rate (mmol/min)/(g protein/L)	Maximum performance per unit luminous flux (mmol/min)/(g protein/L)/(W/m^2)
Cylindrical			
Incandescent bulb	0.04	0.136	0.39×10^{-3}
LED_{710}	0.02	0.107	7.3×10^{-3}
LED_{710} & Fluorescent lamp	0.03	0.115	5.5×10^{-3}
Plate-type			
Incandescent bulb	0.11	0.662	0.79×10^{-3}
LED_{710}	0.06	0.645	2.45×10^{-2}

Note: 1) All the values were determined at the cell concentration of 200 mg protein/L. Removal rate of H_2S was dependent on illuminance, cell and sulfur concentration.
2) Luminous efficacies for incandescent light bulb (200 W) and fluorescent lamp (20 W) were about 20 and 64 lux·m^2/W, respectively [Amick, 1987]. Illuminated surface area of 4-L reactor was 0.249 m^2.

Light Source

In a 4-L cylindrical fermentor, the maximum specific growth rate was 0.016 h^{-1} in 51 h at an initial cell loading of 107 mg protein/L with 128 LEDs of 1.8 W. A considerable increase of maximum specific growth rate to 0.04 h^{-1} was resulted in with 384 LEDs of 3.6 W similar to those of incandescent light. Maximal sulfide removal rate was 0.107 h^{-1} less than that with incandescent light sources.

When the LEDs of total electric consumption of 3.6 W and additional fluorescent light of 400 lux were used as the light source, maximum specific growth rate was 0.03 h^{-1}. Removal rate of H_2S was about 0.115 mmol·L/min·g protein, slightly improved in comparison with a single light source of LED's.

In the current plate-type reactor, maximal specific growth rate increased from 0.04 h^{-1} in the cylindrical reactor to 0.11 h^{-1} with the incandescent light sources. It increased from 0.02 h^{-1} in the cylindrical reactor to 0.06 h^{-1} in the plate-type reactor with LEDs. Improvement ratio of 2.75 (0.11/0.04) with the incandescent light is a slightly less than 3.0 (0.06/0.02) with the LED's, which is due to less uniform illumination in the cylindrical fermentor as explained earlier.

The variation of cell and sulfide concentration in the media with LED's light source shows a similar pattern as those with the incandescent light sources (Fig. 6). But the sulfate concentration remains at a low level, which means that the light intensity with the LED's array was not strong enough to carry out oxidation reaction by Eq. (2). Although the illumination is uniform over the wall, its absolute intensity seems to be not sufficient for penetrating into the deep region of the plate-type reactor. And LED arrays are constant with the cell growth (Fig. 4).

Table 2 summarizes the specific growth rate, H_2S removal rate per unit protein, and maximum performance per unit protein for both types of cylindrical and plate reactors with different light sources. Maximum specific growth rate of the incandescent light source was greater than that of LEDs, but maximum performance per unit luminous flux of LEDs was 16 times greater than that of incandescent lights. Light energy saving was 99% with LEDs, and is similar to the previous work (4). Comparing the current results with those of the conventional fermentor, specific growth rate increased over 2 times, maximum H_2S removal rate per unit protein increased by a factor of 5, and maximum performance per unit luminous flux increased by a factor of 2. For the gas-lift reactor, the transmitting area of one wall of the reactor is 1,185 cm^2. And the surface area of the 4-L fermentor in the previous work was 1,900 cm^2.

More electric consumption could be anticipitated depending on the recent progressive studies on blue-LED and flexible LED [Gustafsson, 1992]. Further reduction of light energy will be possible also with the sunlight in the daytime.

CONCLUSION

A photosynthetic bacterium *C. thiosulfatophilum* absorbs light strongly at 460 nm and 760 nm. In order to reduce light energy consumption, light emitting diode which emits light maximum at 710 nm was applied as an alternative light source to incandescent light. The geometry of surface-to-volume was increased by substituting the conventional cylindrical type for the plate-type one. Sulfide removal rate per unit mg protein in the plate-type reactor was five times as that in the conventional cylindrical fermentor. And the light energy efficiency was enhanced two times in the plate-type reactor with the same LED light source.

The advantage of this 2-dimensional gas-lift reactor is that the reactor volume can be increased simply by increasing its height. If the height is increased, the residence time of hydrogen sulfide gas in the reactor is also increased. So greater aspect ratio is desirable.

ACKNOWLEDGEMENT

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