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REMOVAL OF HYDROGEN SULFIDE IN A THREE PHASE FLUIDIZED BED BIOREACTOR

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Abstract – To remove hydrogen sulfide biologically, a three phase fluidized bed bioreactor was used in which *Thiobacillus* sp.IW was immobilized on biosands. The optimum operating condition of the bioreactor was found to be 30 °C, pH 7, bed height of 0.85-1.0 m and aspect ratio of 1.0. At these conditions, the bioreactor removed more than 88 % of the hydrogen sulfide for an inlet concentration of 30-160 ppm and a gas flow rate of 2-5 *l*/m. The maximum removal rate obtained was about 1,000 mg H_2S/min. In continuous operation of the bioreactor, the removal efficiency remained at 99 % for up to 16 hours and decreased to 91 % at 52 hours.

Key words: Hydrogen Sulfide, *Thiobacillus* sp.IW, Immobilization, Three Phase Fluidized Bed Bioreactor, Removal Rate

INTRODUCTION

Odor from waste water treatment plants and petrochemical plants is highly toxic and harmful to human health. One of the most abundant components present in the odor is hydrogen sulfide (H_2S) [Yang and Lee, 1994]. H_2S has conventionally been removed by techniques based on absorption and adsorption [Chang and Shin, 1993; Barth, 1984]. In recent research, biological processes using sulfur oxidizing microbes removed H_2S at a low operating cost and high removal efficiency without significant secondary contaminations [Sublette and Sylvester, 1987; Tanji et al., 1989; Janssen et al., 1996].

Sulfur oxidizing microorganisms can be largely divided into aerobic and anaerobic bacteria. The aerobic microbes that oxidize H_2S to S, SO_3^{2-} and SO_4^{2-} depending on sulfur concentration are *Thiobacillus, Pseudomonas, Beggiatoa, Thiotrix, Thiomicrospira, Hyphomicrobium* [Brock and Madigan, 1991]. *Thiobacillus* species are popular in small scale operation because *Thiobacillus* species oxidize a variety of sulfur compounds including H_2S, S, and $S_2O_3^{2-}$, grow over a wide range of temperature and pH and show relatively fast growth rate. *Thiobacillus* species employed to remove H_2S are *T. thioparus, T. thiooxidans, T. ferooxidans, T. denitrificans, T. intermedius* and *T.* sp [Ryu, 1996; Cho et al., 1991; Chung et al., 1996; Huang et al., 1996].

In anaerobic conditions, phototrophic bacteria such as *Chlorobium, Chromatium* and *Ectothiorhodospira* convert H_2S to S and SO_4^{2-} depending on light intensity [Kim and Chang, 1991; Kusai and Yamanaka, 1973; Then and Truper, 1983]. However, there are significant problems in using phototrophic bacteria in a large scale operation due to anaerobic growth conditions, very slow growth rate and the need for a strong light source.

In this study, a three phase fluidized bed bioreactor, in which *Thiobacillus* sp.IW is immobilized on biosands, is used to remove H_2S effectively; removal efficiencies and removal rates are measured for the inlet H_2S concentrations of 30-350 ppm, gas flow rates of 2-5 *l*/min, temperatures of 20-40 °C, pHs of 6-8, bed heights of 0.5-1.0 m and aspect ratios of 0.5-4.0. *Thiobacillus* sp.IW [Cha et al., 1994] used in the study as sulfur oxidizing bacteria showed optimum growth at 30 °C, pH 7 and cell doubling time was 38 min in the exponential growth period for the optimum condition [Kim et al., 1996], which is exceptionally fast compared with other sulfur oxidizing bacteria [Tabita and Lundgren, 1971; Cho et al., 1991]. The three phase fluidized bed bioreactor consisted of a gas phase (H_2S and air), a liquid phase (cell and medium) and a solid phase (cell and carrier). Rising bubbles and moving carriers in the bioreactor increase the contact between the microbes and H_2S, which increases the oxygen mass transfer to the bacteria. Therefore, the bioreactor is suitable for removal of large volumes of H_2S.

EXPERIMENTAL

1. Cell Culture and Immobilization

Thiobacillus sp.IW [Cha et al., 1994] was isolated from the acid drainage water from coal mines (Hwasoon, Korea) as a sulfur oxidizing bacterium. The composition of the cell medium was shown in Cha et al. [1994], and dissolved $Na_2S_2O_3$ instead of H_2S was used as an energy source for the bacteria in liquid culture. The basic medium and yeast extract solution were autoclaved separately and the pH of the mixture was adjusted by either NaOH or HCl.

To maintain high efficiency in the bioreactor, *Thiobacillus*

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Table 1. Physical properties of biosands, bioceramics and activated carbon

	Activated carbon	Biosands	Bioceramics
Media size (mm)	0.84-1.68	2.0-3.0	1.6-2.2
Density (g/cm^3)	1.37	1.27	2.2
Specific surface area (m^2/g)	936	539	1.47
Total pore area (m^2/g)	956	589	0.27
Pore volume (m^3/g)	97.7	740	2.81

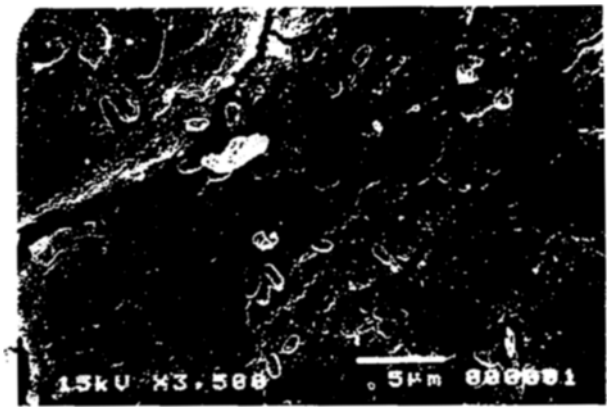

Fig. 1. SEM photograph of *Thiobacillus* sp.IW immobilized on biosands (×3,500).

sp.IW was immobilized on three kinds of carriers, such as biosands, bioceramics and activated carbons. Physical properties of carriers used in this study are shown in Table 1 and an SEM photograph of *Thiobacillus* sp.IW immobilized on biosands is shown in Fig. 1. After activation of *Thiobacillus* sp.IW, 1 ml of culture medium including the bacteria (2×10^9 cells/ml medium) was added to 99 ml fresh medium in 250 ml flask which contained 7.5 g of carriers. The solution was shaken for 24 hours at 30 °C, pH 7 before cells were moved to the bioreactors.

2. Three Phase Fluidized Bed Bioreactor

A three phase fluidized bed bioreactor (Fig. 2) was used to remove H_2S effectively. Carriers immobilized by *Thiobacillus* sp.IW and cell medium were placed in the bioreactor. The air from the compressor and H_2S from a gas tank were mixed in a mixing chamber and diluted H_2S was allowed to enter at the bottom of the fluidized bed. The carriers were fluidized by gas flow and the bacteria either in solution or on the carrier oxidized H_2S; the remaining gas left at the top of the column. To maintain a controlled temperature, constant temperature water was circulated outside of the gas mixing chamber and of the bioreactor.

The inner diameter of the bioreactor was 4 cm and the height of the bioreactor column was 130 cm. The working volume of the bioreactor was 1,256 cm^3 with a liquid height in the bed of 100 cm. The distributor which had 85 holes of 1 mm diameter was installed in bottom of the column for uniform gas distribution and to prevent the loss of carriers. The inlet and outlet concentrations of H_2S were measured at the port by a gas monitor (Neotronics, Takeley, UK).

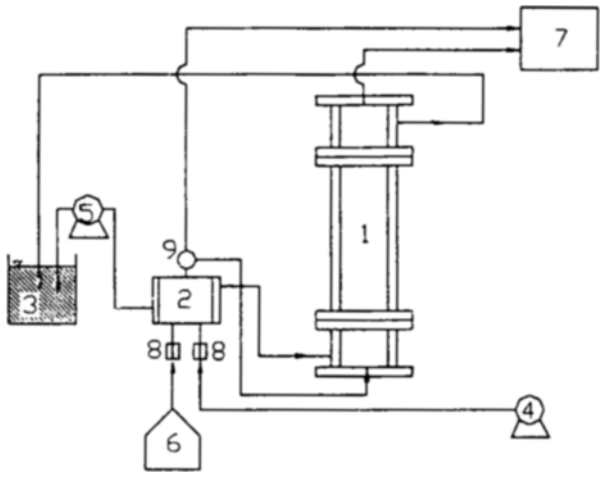

Fig. 2. Schematic diagram of three phase fluidized bed bioreactor.

1. Bioreactor
2. Gas mixing chamber
3. Water bath
4. Air compressor
5. Circulation pump
6. H_2S bomb
7. Gas analyzer
8. Flowmeter
9. Three way valve

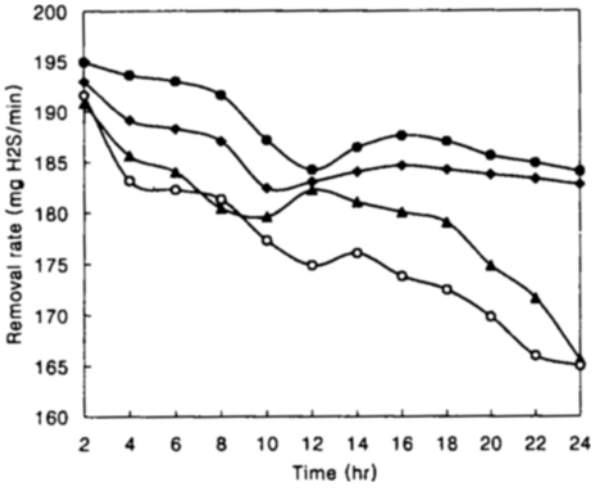

Fig. 3. H_2S removal rate of two phase fluidized bed bioreactor without immobilization (○) vs. that of three phase fluidized bed bioreactors with carriers of biosands (●), bioceramics (◆), activated carbons (▲) at concentration of 200 ppm, gas flow rate of 1 l/min, 30 °C, pH 7, bed height of 1.0 m and L/D of 1.0.

RESULTS AND DISCUSSION

In Fig. 3, the H_2S removal rate (= $C_{in}\cdot Q\cdot\eta$) of a two phase fluidized bed bioreactor without immobilization is compared with that of three phase fluidized bed bioreactors with carriers of biosands, bioceramics and activated carbons. The removal rate of the three phase fluidized bed bioreactors is higher than that of two phase fluidized bed bioreactor. Among the three different carriers, the bioreactor immobilized on biosands shows highest the removal rate since the pore volume of the biosand has the highest value among the tested carriers (Table

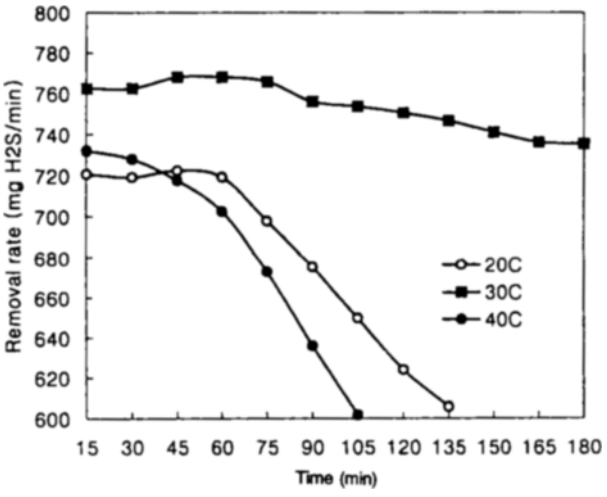

Fig. 4. H_2S removal rate of three phase fluidized bed bioreactor immobilized on biosands with the temperature change at concentration of 160 ppm, gas flow rate of 5 *l*/min, pH 7, bed height of 1.0 m and L/D of 1.0.

1). Therefore, for all the experiments in the three phase fluidized bed bioreactor, biosands were used as carrier material.

Fig. 4 shows the effect of temperature on the removal rate and the optimum temperature of the bioreactor is 30 °C for the growth of *Thiobacillus* sp.IW. With a pH change of 6-8, the bioreactor exhibits the highest removal rate at pH 7 that is the optimum pH for the bacteria [Son, 1997].

Fig. 5 shows the removal rate with a variation of liquid bed height of 0.5-1.0 m. The removal rate is 119 mg H_2S/min with a bed height higher than 0.85 m, whereas the removal rate decreases to 113 mg H_2S/min with a bed height of 0.5 m for 3 hour operation. As the bed height of the bioreactor increases from 0.5 m to 0.85 m, the residence time of the inlet H_2S and the number of cells in the bioreactor increase; therefore, the removal rate of H_2S increases. The removal rate of H_2S does not increase further when the bed height changes

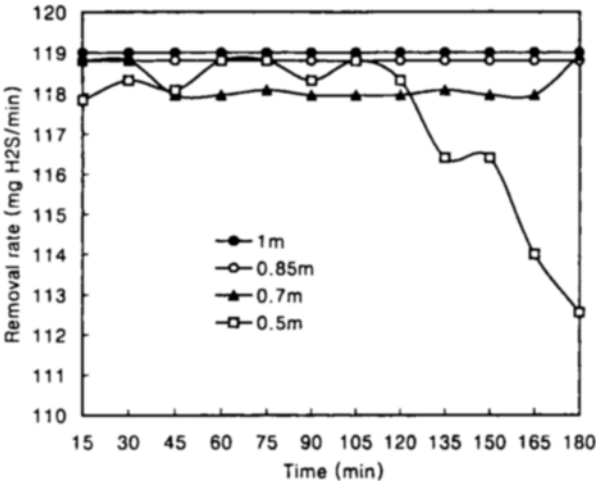

Fig. 5. H_2S removal rate of three phase fluidized bed bioreactor immobilized on biosands with the bed height change at concentration of 60 ppm, gas flow rate of 2 *l*/min, 30 °C, pH 7 and L/D of 1.0.

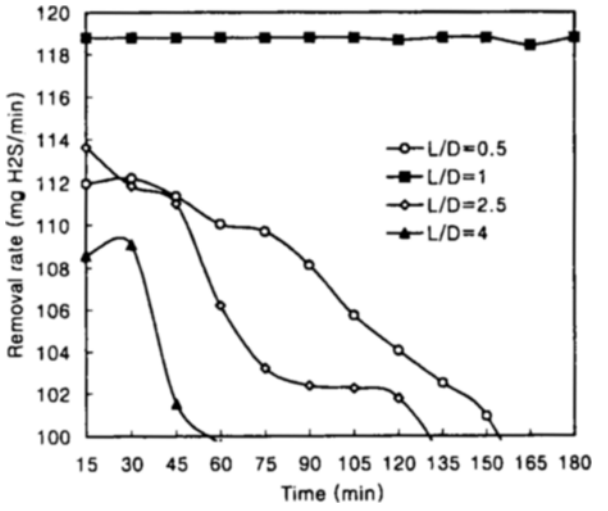

Fig. 6. H_2S removal rate of three phase fluidized bed bioreactor immobilized on biosands with the aspect ratio (L/D) change at concentration of 60 ppm, gas flow rate of 2 *l*/min, 30 °C, pH 7 and bed height of 1.0 m.

from 0.85 m to 1.0 m because the removal efficiency of H_2S is already near 100 % at a bed height of 0.85 m.

Fig. 6 shows the effect of aspect ratio (L/D) on the removal rate. The removal rate is highest at an aspect ratio of 1.0, that is, the height of packed carriers before fluidization is the same as the diameter of the bioreactor since it has been known that solid mixing is the highest at L/D=1.0. For an aspect ratio lower than 1.0, the number of carriers in the bioreactor is not enough for fluidization. When the aspect ratio increases further from 1.0, the number of carriers increases and fluidization is hindered; thus the bioreactor becomes more like a packed bed. From Fig. 6, it is clear that the three phase fluidized bed bioreactor is more effective than the biofilter system.

At optimum operating conditions such as 30 °C, pH 7, bed height of 1.0 m and aspect ratio of 1.0, the removal rate of

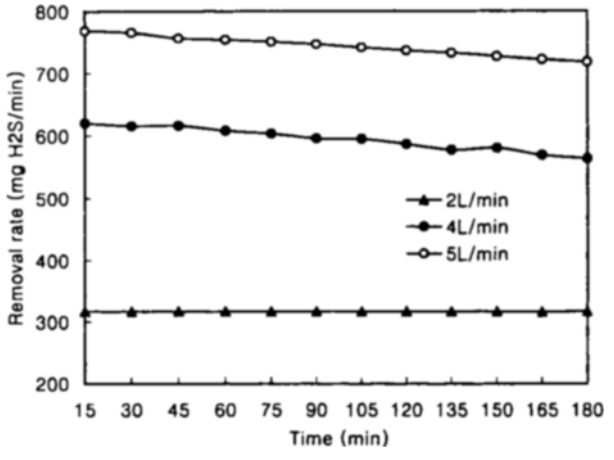

Fig. 7. H_2S removal rate of three phase fluidized bed bioreactor immobilized on biosands with the gas flow rate change at concentration of 160 ppm, 30 °C, pH 7, bed height of 1.0 m and L/D of 1.0.

the three phase fluidized bed bioreactor is measured at an inlet concentration of 30-350 ppm and inlet gas flow rate of 2-5 *l*/min. At an H_2S inlet concentration of 30 and 60 ppm, gas flow rate of 2-5 *l*/min, the removal efficiency [$\eta=(C_{in}-C_{out})/C_{in}$] for 3 hours is more than 0.99 and the removal rate obtained is 59.4-297 mg H_2S/min [Son, 1997].

Fig. 7 shows the removal rate at a concentration of 160 ppm. The removal rate increases as the gas flow rate increases. At a gas flow rate of 4-5 *l*/min, the removal rate decreases in time as the removal efficiency decreases from 0.99 to 0.88-0.90, since the amount of inlet H_2S is near the potential capacity of the bioreactor and the residence time of inlet H_2S is shorter in higher gas flow rates.

Fig. 8 shows the removal rate at a concentration of 350 ppm. Up to a gas flow rate of 3 *l*/min, the bioreactor shows stable performance; however, the removal rate reduces significantly at a gas flow rate of 5 *l*/min after 150 min. One possible explanation for the sudden drop of the removal rate is that the amount of inlet H_2S is much higher than the potential capacity of the bioreactor. From Fig. 8, the maximum stable removal rate of the bioreactor for 3 hour operation is ~1,000 mg H_2S/min.

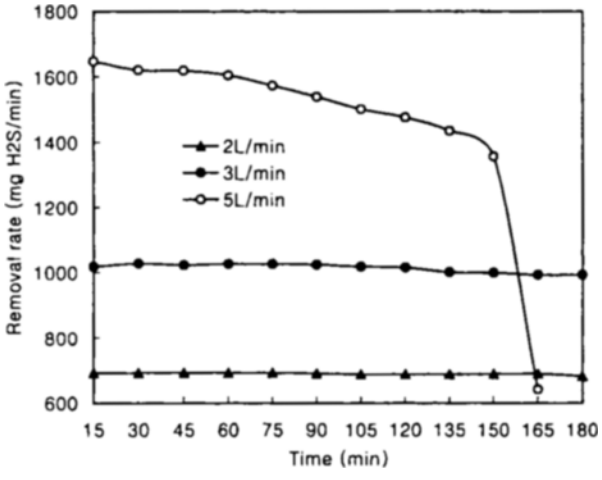

Fig. 8. H_2S removal rate of three phase fluidized bed bioreactor immobilized on biosands with the gas flow rate change at concentration of 350 ppm, 30 °C, pH 7, bed height of 1.0 m and L/D of 1.0.

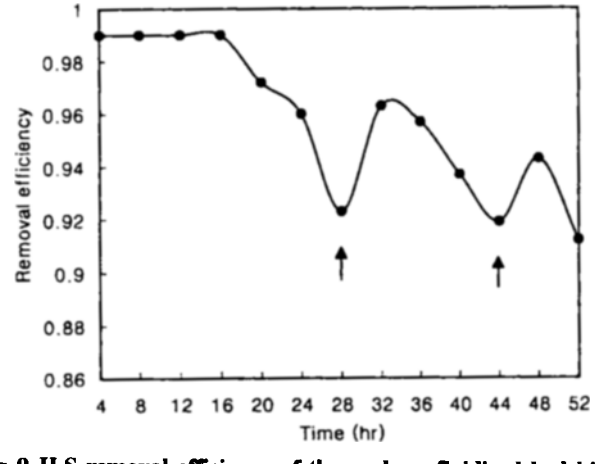

Fig. 9. H_2S removal efficiency of three phase fluidized bed bioreactor immobilized on biosands with continuous operation at concentration of 60 ppm, gas flow rate of 2 *l*/min, 30 °C, pH 7, bed height of 1.0 m and L/D of 1.0.

Fig. 9 shows the removal efficiency of the bioreactor for continuous operation. The removal efficiency is maintained at 0.99 for up to 16 hours and decreases to 0.91 at 52 hours due to the depletion of the essential components in the cell medium and the accumulation of cell exhaust. At 28 hours and 44 hours after the initial operation, components of cell medium as shown in Cha et al. [1994] are added in the solution of the bioreactor; the efficiency increases slightly afterward as shown in the figure since the cell growth condition in the bioreactor is improved due to the addition of carbon and mineral sources essential to cells.

CONCLUSION

From this study, the removal rate of H_2S is measured in a three phase fluidized bed bioreactor with cell carriers such as biosands, bioceramics and activated carbons. The bioreactor immobilized on biosands shows the highest removal rate. The optimum operating conditions of the bioreactor are 30 °C, pH 7, bed height of 0.85-1.0 m and aspect ratio of 1.0. At the optimum condition, the bioreactor immobilized on biosands exhibits more than 0.88 removal efficiency during 3 hour operation for an inlet H_2S concentration of 30-160 ppm, gas flow rate of 2-5 *l*/m. The maximum stable removal rate of the bioreactor obtained at an H_2S concentration of 350 ppm and a gas flow rate of 3 *l*/m is ~1,000 mg H_2S/min. In continuous operation of the bioreactor, the removal efficiency remains at 0.99 for up to 16 hours and decreases to 0.91 at 52 hours. From this study, it is shown that the three phase fluidized bed bioreactor immobilized with *Thiobacillus* sp.IW on biosands is suitable for removing lower concentrations of H_2S.

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NOMENCLATURE

C_{in} : inlet concentration of H_2S [ppm]
C_{out} : outlet concentration of H_2S [ppm]
D : diameter of three phase fluidized bed bioreactor column [cm]
L : height of packed carriers before fluidization [cm]
Q : volumentric gas flow rate [*l*/min]
η : removal efficiency [$(C_{in}-C_{out})/C_{in}$]

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