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Simultaneous Removal of Hydrogen Sulfide and Ammonia Using *Thiobacillus* sp. IW in a Three-Phase Fluidized-Bed Bioreactor

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Abstract A three-phase fluidized-bed bioreactor including *Thiobacillus* sp. IW was tested to remove H_2S and NH_3 simultaneously. The inlet H_2S was oxidized to SO_4^{2-} by *Thiobacillus* sp. IW, and the NH_3 reacted with the SO_4^{2-} to form $(NH_4)_2SO_4$. The removal efficiency of H_2S was 98.4–99.9% for an inlet concentration of 36–730 ppm and that of NH_3 was 60.2–99.2% for an inlet concentration of 45–412 ppm. The removal efficiency of NH_3 was reduced when the inlet loading rate of NH_3 was increased above 10 mg/l/h. When the bioreactor was operated for 25 days with a lower inlet concentration of NH_3 compared with that of H_2S, the bioreactor exhibited an excellent performance with a stable pH, dissolved oxygen content, and cell concentration.

Key words: *Thiobacillus* sp. IW, hydrogen sulfide, ammonia, removal efficiency, loading rate

Odors from petrochemical plants, wastewater treatment plants, and sanitary landfills contain many toxic chemicals which are either organic or inorganic compounds. Among the inorganic chemicals, sulfurous compounds including hydrogen sulfide (H_2S) and nitrogen compounds such as ammonia (NH_3) are the most abundant [2, 19]. Odorous gases have been conventionally removed by physical and chemical treatments like absorption, adsorption, and catalytic oxidation [3, 5]. However, these methods have certain problems such as a low removal efficiency, high operating cost, and secondary contamination [4].

With biological treatments, H_2S and NH_3 can be simultaneously removed using various types of bioreactors. Heijnen *et al.* [7] used an anaerobic-aerobic biofilm reactor to treat industrial wastewater including H_2S and NH_3, however, the system is too complicated to operate on a large scale. Scheels and Park [16] used a soil bed biofilter including ground used tires, however, it showed insufficient capacity under dry conditions. Fouhy [6] used trickling filters to remove waste gases including amines, alcohol, H_2S, and NH_3. Accordingly, the results from previous studies have been either too low in removal efficiency or unsuitable for treating large volumes of gas. Even though many studies have been conducted on the biological removal of H_2S [8, 10, 12] or NH_3 [13, 18], studies on the simultaneous biological removal of H_2S and NH_3 are scarce.

In this research, H_2S and NH_3 were simultaneouly removed using a three-phase fluidized-bed bioreactor [17] including *Thiobacillus* sp. IW, which exhibited an excellent removal efficiency for H_2S [9]. In the bioreactor, the H_2S was oxidized to SO_4^{2-} by the microbes and NH_4^+ then reacted with the generated SO_4^{2-} to form $(NH_4)_2SO_4$. The reactions that took place in the bioreactor can be shown as follows:

$$H_2S+2O_2 \rightarrow SO_4^{2-}+2H^+ \quad (1)$$

$$NH_3+H^+ \rightarrow NH_4^+ \quad (2)$$

$$2NH_4^++SO_4^{2-} \rightarrow (NH_4)_2SO_4 \quad (3)$$

The removal capacity of H_2S and NH_3 was measured for 36–730 ppm H_2S, 45–412 ppm NH_3 and a gas flow rate of 120–240 l/h. The removal efficiency of H_2S and NH_3 was also measured during 25 days of continuous operation to check the stability of the bioreactor.

Thiobacillus sp. IW, which was isolated from acid drainage water from coal mines in Hwa-Soon, Korea by Prof. In-Wha Lee of Chosun University, was used throughout this study [1]. The *Thiobacillus* sp. IW showed an optimum growth at 30°C, pH 7.0 and was cultured in the following medium (g/l): 8.0 $Na_2S_2O_3$, 0.5 NH_4Cl, 4.0 K_2HPO_4, 4.0 KH_2PO_4, 0.8 $MgSO_4$, 0.5 Na_2EDTA, 0.22 $ZnSO_4$, 0.05 $CaCl_2$, 0.01 $MnCl_2 \cdot 4H_2O$, 0.05 $FeSO_4$, 0.01 $(NH_4)_6Mo_7O_{24}$, 0.01 $CuSO_4$, 0.01 $CoCl_2$, and 2.0 yeast extract. Basic medium and yeast extract solution were autoclaved separately for 15 min and the pH of the mixture was adjusted to 7.0 by 1 M HCl. To increase the mixing in the solution (to fluidize solution), biosands (Crystal bio-sand, Chungwoo art system, Seoul, Korea) composed of 15% SiO_2 and 85% H_2O with a specific surface area of 539 m^2/g were added in

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the bioreactor as carriers. To adapt the cells in the fluidized-bed bioreactor, low concentrations of H_2S and NH_3 were introduced and the bioreactor reached a steady state after 5 days of operation. The cell concentration in the bioreactor was maintained at about 1×10^9 cells/ml solution.

A three-phase fluidized-bed bioreactor, as shown in Fig. 1, was used to remove H_2S and NH_3. The H_2S and NH_3 from each gas tank were diluted with air to an appropriate concentration in a mixing chamber before entering the fluidized-bed bioreactor (inner diameter = 5 cm, height = 130 cm). The inlet gas fluidized the carriers, the bacteria in both the carriers, and the solution then oxidized the H_2S. The NH_3 was then removed by the reaction with the generated SO_4^{2-}. An aeration unit (inner diameter = 14 cm, height = 15 cm) was installed in the bioreactor system to circulate the solution. The liquid-phase height of the column was 60 cm and the mean residence time of the inlet gas in the solution was 17.7-35.3 sec. The total volume of the solution including the bioreactor and aeration unit was 2.5 l. To control the temperature of the reactor solution, constant temperature water was circulated outside of the bioreactor and aeration unit. A distributor with 85 of 1 mm-diameter holes was installed in the bottom of the column to maintain a uniform gas distribution and prevent the loss of the carriers. The optimum operating condition of the bioreactor was 30°C, pH 7.0, with 101 g biosands/5 cm diameter, which was determined in a previous research [14].

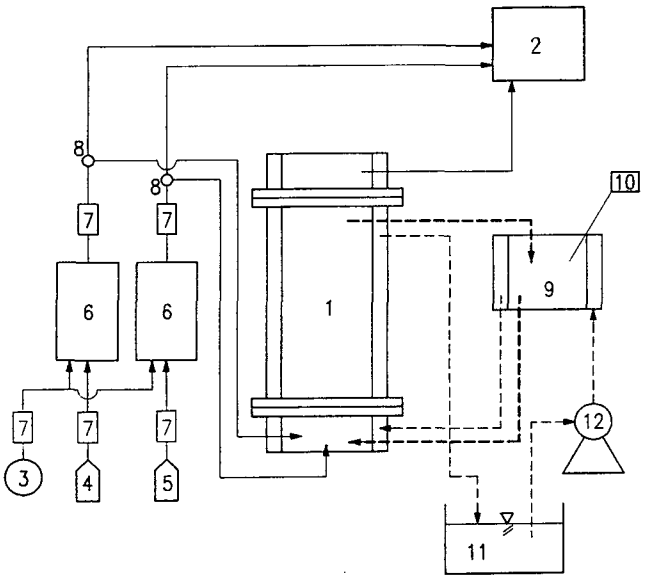

Fig. 1. Schematic diagram of the three-phase fluidized-bed bioreactor.

The concentration of H_2S was measured by a gas chromatograph (Donam Instrument, Seoul, Korea) equipped with a pulse discharge detector (Valco Instruments, Houston, U.S.A.) and GS-Q column. The oven temperature was increased from 40°C to 110°C in 12 min, the injector was maintained at 110°C, and the detector temperature was 160°C. He gas with a flow rate of 8 ml/min was used as the carrier gas. The minimum detection limit of H_2S in the gas chromatograph was 0.1 ppm. The NH_3 concentration was estimated by measuring the absorbance of the indophenolblue of the mixed solution at 640 nm (Shimadsu, Tokyo, Japan) [11]. The minimum detection limit of NH_3 in this study was 0.5 ppm. The concentration of $(NH_4)_2SO_4$ in the bioreactor solution was measured using the salicylate method [15] with an autoanalyzer (Bran+Luebbe, Norderstedt, Germany).

In this study, the removal efficiency, inlet loading rate, and removal capacity were calculated according to the following formulae;

$$\text{Removal efficiency } (\eta) = (C_{in} - C_{out})/C_{in} \quad (4)$$

$$\text{Inlet loading rate} = C_{in}Q/V \text{ [mg/l/h]} \quad (5)$$

$$\text{Removal capacity} = \eta\, C_{in}Q/V \text{ [mg/l/h]} \quad (6)$$

Figure 2 shows the variation of the optical density of reactor solutions in a 24 h flask culture of *Thiobacillus* sp. IW with respect to $(NH_4)_2SO_4$ concentration, and the optimum concentration was identified as 5 g $(NH_4)_2SO_4$/l. Compared with the cell growth in the basic medium, which did not include $(NH_4)_2SO_4$, $(NH_4)_2SO_4$ had a positive effect on the cell growth up to 15 g/l.

Figure 3 shows the removal efficiencies of H_2S and NH_3 with and without microorganisms in the bioreactor. Without the cells, H_2S and NH_3 were partially removed due to their absorption in the solution. The absorption of NH_3 was reported to increase when the concentration of aqueous negative ion was increased and the solution became acidic

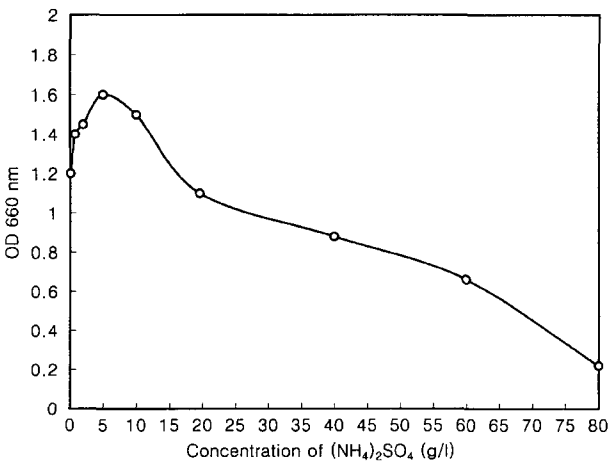

Fig. 2. Variation of the optical density of the solution in a 24 h flask culture of *Thiobacillus* sp. IW with respect to $(NH_4)_2SO_4$ concentration.

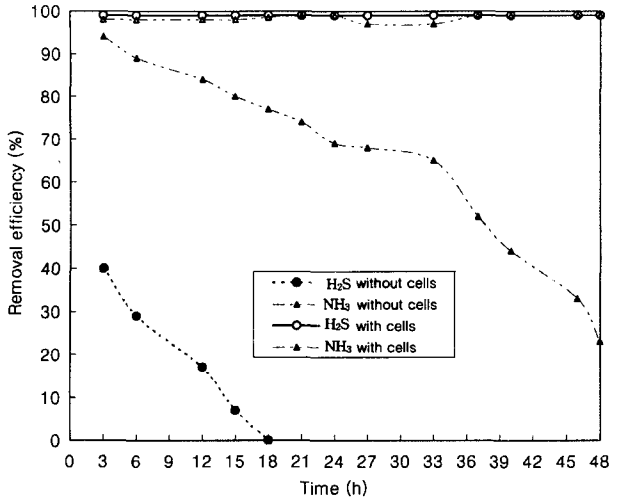

Fig. 3. Removal efficiency of H_2S and NH_3 with and without cells.
$C_{in}(H_2S)$ = 178 ppm, $C_{in}(NH_3)$ = 170 ppm, and Q = 120 l/h.

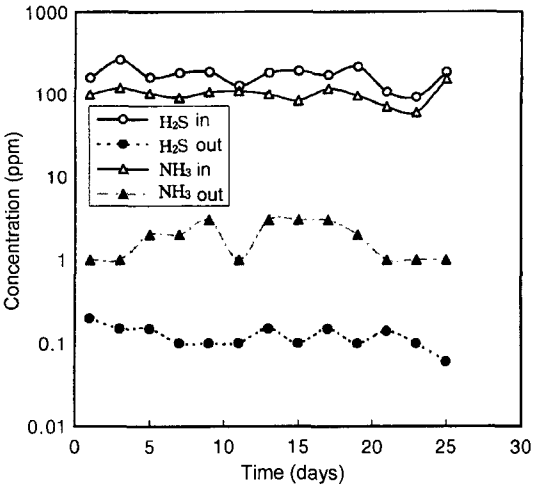

Fig. 5. Inlet and outlet concentration of H_2S and NH_3 in a continuous operation.
$C_{in}(H_2S)$ = 91-260 ppm, $C_{in}(NH_3)$ = 60-151 ppm, and Q = 120 l/h.

[20]. However, the removal efficiencies of H_2S and NH_3 were reduced significantly with time as the gases became saturated in the solution. The difference between the removal efficiency with and without the cells was the contribution of *Thiobacillus* sp. IW in the bioreactor. Therefore, all the experimental data shown in this study were obtained from operations longer than 5 days from the initial start of the bioreactor; as such, all the removal of H_2S and NH_3 was due to the cells in the bioreactor.

Figure 4 shows the simultaneous removal capacities relative to the loading rate of H_2S and NH_3 and all data are based on the average of a 12-24 h operation. The removal efficiency of H_2S was 98.4-99.9% for an inlet concentration of 36-730 ppm and that of NH_3 was 60.2-99.2% for an inlet concentration of 45-412 ppm. The removal efficiency of H_2S was extremely high due to high cell concentration to oxidize H_2S to SO_4^{2-}. However, the removal efficiency of NH_3 reduced as the loading rate increased above 10 mg/l/h. The fact that the lower removal efficiency of NH_3 was related with the formation of $(NH_4)_2SO_4$ can be proved with the experimental observation that the removal efficiency for NH_3 was always lower when a stoichiometrically excess amount of NH_3 compared with H_2S entered the bioreactor. The maximum removal capacities obtained in this study were 48.7 mg/l/h for H_2S and 17.7 mg/l/h for NH_3, respectively.

The inlet and outlet concentrations of H_2S and NH_3 were measured continuously for 25 days under a lower inlet concentration of NH_3 compared with that of H_2S, as shown in Fig. 5. For the inlet concentration range tested, the outlet concentration of H_2S was 0.06-0.15 ppm, and that of NH_3 was 1-3 ppm. The bioreactor satisfied the emission standard of the Ministry of Environment, Korea which is 0.2 ppm for H_2S and 5 ppm for NH_3 in an industrial area. During the operation, the pH, dissolved oxygen content, and cell concentration maintained a steady state and the concentration of $(NH_4)_2SO_4$ generated in the bioreactor increased monotonically from 0 to 11.2 g/l, as indicated in Table 1. Accordingly, this study showed that a three-phase fluidized-bed bioreactor including *Thiobacillus* sp. IW had an excellent ability to remove H_2S and NH_3 simultaneously in a region where the generation of NH_3 was relatively low.

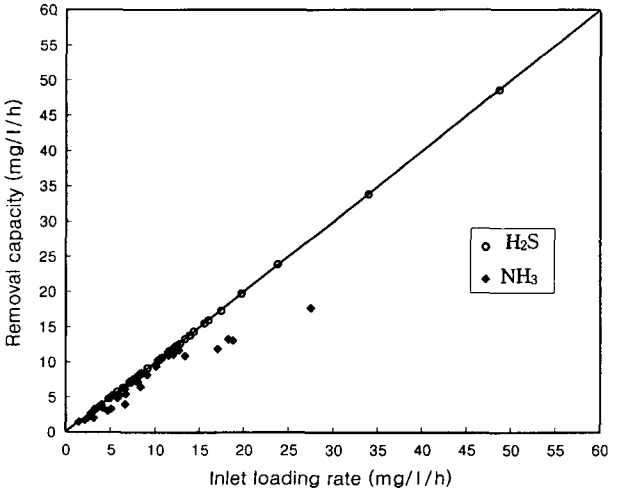

Fig. 4. Removal capacity of the bioreator with inlet loading rates of H_2S and NH_3.
$C_{in}(H_2S)$ = 36-730 ppm, $C_{in}(NH_3)$ = 45-412 ppm, and Q = 120-240 l/h.

Table 1. pH, dissolved oxygen content, and concentrations of cell and $(NH_4)_2SO_4$ for continuous 25 days of operation.

pH	6.5-6.6
Dissolved oxygen content (mg/l)	8.0-8.8
Cell concentration (cells/ml)	$8.0-11\times10^8$
Concentration of $(NH_4)_2SO_4$	0→11.2 g/l

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Nomenclatures

C_{in} : inlet concentration [ppm]
C_{out} : outlet concentration [ppm]
Q : gas volumetric flow rate [l/h]
V : volume of solution in the bioreactor system [2.5 l]
η : removal efficiency of odor gases

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