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Microbial Oxidation of Hydrogen Sulfide in a Pilot-Scale Bubble Column

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Thiobacillus denitrificans is a chemoautotroph and a facultatively anaerobic bacterium that can use reduced sulfur compounds as energy sources with oxidation to sulfate. Under anoxic conditions, nitrate may serve as a terminal electron acceptor with reduction to elemental nitrogen. *T. denitrificans* has previously been shown to remove hydrogen sulfide from sour gases under both aerobic and anoxic conditions. Hydrogen sulfide concentrations were reduced from 10 000 ppmv to undetectable levels with 1–2 s of gas–liquid contact time in bench-scale fermentors. The oxidation product, sulfate, accumulated in the liquid phase of the culture medium. Flocculated *T. denitrificans* has now been used to remove hydrogen sulfide (up to 1500 ppmv) from a sour gas in a 0.5-m^3 pilot-scale bubble column. The bubble column was operated for 7 weeks under aerobic conditions, with gas feeds of air and hydrogen sulfide in nitrogen. Up to 97% removal of hydrogen sulfide was observed with complete oxidation to sulfate, which accumulated in the reactor medium. Limitations in H_2S removal were due to mass transfer and not the microbiology of the system. More complete H_2S removal can be accomplished by increasing gas–liquid contact in a single reactor or using two bubble columns in series.

Introduction

A process for the desulfurization (H_2S) of gases based on the contact of a sour gas with a culture of the sulfide-oxidizing bacterium, *Thiobacillus denitrificans*, has been developed. *T. denitrificans* is a strict autotroph and facultative anaerobe first described in detail by Baalsrud and Baalsrud (1954). Sulfide, elemental sulfur, and thiosulfate may be used as energy sources with oxidation to sulfate. Under anoxic conditions, nitrate may be used as a terminal electron acceptor with reduction to elemental nitrogen.

Sublette and Sylvester (1987a–c) and Sublette (1987) have previously demonstrated that *T. denitrificans* may be readily cultured under aerobic or anoxic conditions on H_2S(g) as an energy source at pH 7.0 and 30 °C. When H_2S (1% H_2S, 5% CO_2, and balance N_2) was bubbled into cultures (2.0 L) previously grown on thiosulfate, H_2S was metabolized with no apparent lag. Hydrogen sulfide concentrations in the outlet gas could be reduced to undetectable levels with 1–2 s of gas–liquid contact time. Under sulfide-limiting conditions, concentrations of total sulfide in the culture media were less than 1 μM. Complete oxidation of H_2S to sulfate was observed. The effect of H_2S loading on reactor performance was also investigated (Sublette and Sylvester, 1987a; Sublette, 1987). In certain experiments the H_2S feed rate was increased in steps until H_2S breakthrough was obtained. At this point, the H_2S feed rate exceeded the rate at which the H_2S could be oxidized by the biomass. This upset condition was characterized by the accumulation of elemental sulfur and inhibitory levels of sulfide in the reactor medium. This upset condition was reversible if the cultures were not exposed to the accumulated sulfide for more than 2–3 h.

A sulfide-tolerant strain of *T. denitrificans* (strain F) was isolated by enrichment (Sublette and Woolsey, 1989). Wild-type *T. denitrificans* is inhibited by sulfide concentrations of 0.1–0.2 mM. However, strain F is tolerant of sulfide concentrations in excess of 2.5 mM.

Sublette and Sylvester (1987c) have also shown that the heterotropic contamination resulting from septic operation of certain *T. denitrificans* cultures has a negligible effect on H_2S oxidation by the organism. The autotrophic medium used to grow *T. denitrificans* contained no organic components to support heterotrophic growth. Apparently organic carbon was obtained from waste products of *T. denitrificans* or cell lysis. Sublette (1989) and Ongcharit and Sublette (1991) have demonstrated that *T. denitrificans* may be flocculated by aerobic coculture with floc-forming heterotrophs from an activated sludge system. An H_2S-active, gravity-settleable floc resulted, which was subsequently used to remove H_2S from a gas in a bench-scale continuous stirred-tank reactor with biomass recycle. Flocculated *T. denitrificans* strain F has now been used to remove H_2S from a synthetic sour gas in a pilot-scale bubble column.

Materials and Methods

Organism and Working Culture. *Thiobacillus denitrificans* (ATCC 23642) was originally obtained from the American Type Culture Collection (Rockville, MD). A sulfide-tolerant strain (strain F) was obtained by enrichment as previously described (Sublette and Woolsey, 1989). *T. denitrificans* strain F was flocculated and cultured on a large scale on thiosulfate as described elsewhere (Ongcharit and Sublette, 1989; Ongcharit *et al.*, 1991; Hasan *et al.*, 1993).

The bubble column reactor used in this study was stainless steel in construction, consisting of a skid-mounted 0.61-m-diameter cylinder, 2.44 m high. The lower 1.83 m was jacketed for temperature control. The bottom of the column was conical (at 30° with respect to the horizontal), with a 2.5-cm drain located at the lowest point. The top of the column was a flat stainless steel

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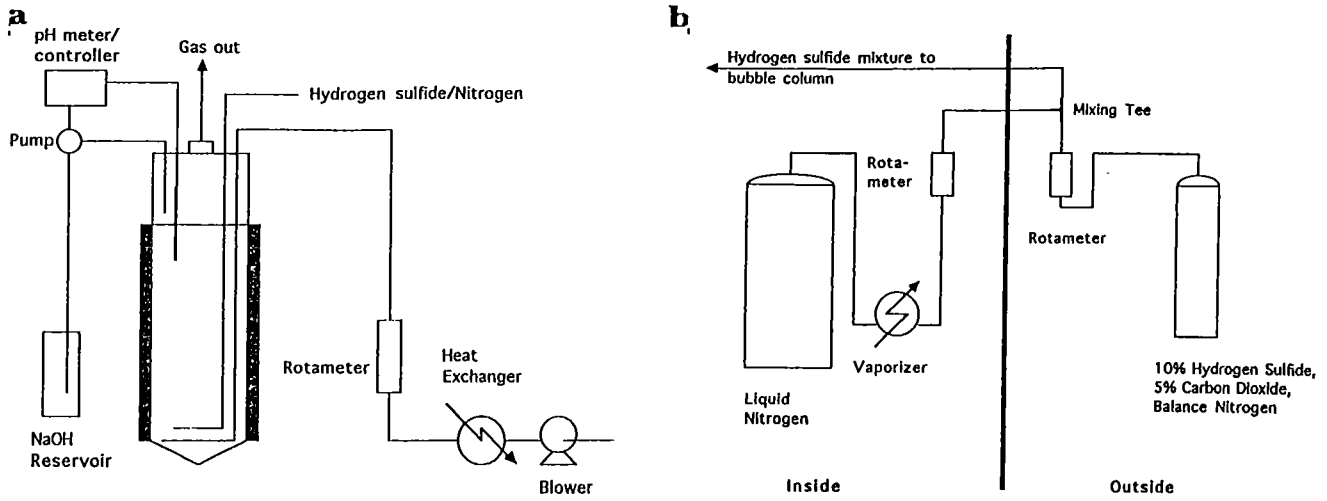

Figure 1. (a) Schematic diagram of the pilot-scale bubble column reactor system. (b) Schematic diagram of the gas blending system to produce sour gas feed for the pilot-scale bubble column.

plate fitted with various threaded couplings for probes, spargers, etc. During initial operation, the inside wall of the column in the jacketed area buckled inward, reducing the actual inside diameter. The actual volume of the column up to the top of the jacket was 0.44 m^3. This gave an average effective column inside diameter of 0.54 m. A schematic diagram of the bubble column is shown in Figure 1a.

The column was fitted with two spargers for gas inlets, each consisting of stainless steel pipe or tubing, which extended through the top plate of the column down to the bottom of the jacketed part of the column. Air was introduced through a 2.5-cm pipe with a 36-cm L (ell) section at the bottom of the column, with 64 3.2-mm holes drilled in the bottom of the L-section. The synthetic sour gas was introduced through a 1.3-cm tube with a 25-cm L-section with 50 3.2-mm holes drilled in the bottom of the L-section. The L-section of the sour gas sparger was located 5 cm above the air sparger and oriented at a 30–40° angle relative to the air sparger. Both spargers were roughly centered in the column. Gases exited the column through a 7.6-cm outlet in the top plate. Exit gases were conveyed via an exhaust fan to a discharge vent on the roof of the building housing the reactor. Air was fed to the column using a Fugi Model VFC 604A-7W ring compressor. Air from the blower was cooled with a Speedair Model 5Z264 after-cooler or heat exchanger using house water at 15 °C. Synthetic sour gas was produced by metering an H_2S source (10% H_2S, 5% CO_2, balance N_2; Big Three Industries, LaPorte, TX) and N_2 to a mixing tee prior to being fed to the bubble column (Figure 1b).

The process culture was maintained at 30 °C by circulating water at this temperature through the jacket from a Neslab Model HX-300 refrigerated recirculator. The pH was monitored and maintained at 7.0 ± 0.05 by a Cole-Parmer (Chicago, IL) Model 5651–50 pH meter/controller, which activated a Cole-Parmer Chem-Feed pump to deliver 50% NaOH (Kjeldahl-N grade, Ricca Chemicals, Arlington, TX) as needed.

At startup, a concentrated suspension of flocculated *T. denitrificans* strain F was diluted with a fresh mineral salts medium (nonsterile) consisting of (in g/L) Na_2HPO_4 (1.2), KH_2PO_4 (1.8), $MgSO_4 \cdot 7H_2O$ (0.4), NH_4Cl (0.5), $CaCl_2$ (0.03), $MnSO_4$ (0.02), $FeCl_3$ (0.02), and $NaHCO_3$ (1.0). This suspension was then pumped into the column, which was filled to the top of the jacket (0.44-m^3 volume and 1.83 m from liquid level to spargers). The initial concentration of biomass or mixed liquor suspended solids (MLSS) was 1.3 g/L. When the temperature reached 30 °C, aeration and sour gas feed were initiated. Aeration rates of 0.057–0.113 m^3/min or 0.13–0.26 ~~$mg^3/min \cdot mL^3$~~ (~~vvm~~) were used. Sour gas feed rates ranged from 0.034 to 0.12 m^3/min with H_2S concentrations of 0.25–2.9 g/m^3. This corresponds to superficial sour gas velocities (based on the effective column diameter) of 0.25–0.87 cm/s. The gas–liquid contact time was estimated to be less than 10 s.

Due to the hazards associated with working with H_2S, the column was operated with H_2S feed for only 8–9 h, 5 days per week, during normal working hours. When not receiving an H_2S feed, the reactor was maintained at 30 °C and aerated at 0.06–0.12 m^3/min of air. The reactor was operated in this way for 198.5 h of actual operating time with various H_2S feeds. At the end of this time, one-half of the reactor contents was drained from the reactor and replaced with fresh medium, resulting in a decrease in the MLSS to 0.5 g/L. The reactor was then operated for an additional 52 h with H_2S feed. At the end of this time, a concentrated suspension of *T. denitrificans* strain F was added to the reactor to bring the MLSS concentration back to about 1.5 g/L. Operation with various H_2S feeds then continued for an additional 51 h.

At the end of this time, the MLSS concentration was 1.65 g/L. The total liquid height (above the spargers) was 1.83 m. An experiment was then conducted to investigate the effect of liquid height on H_2S removal as follows. The column was operated at an aeration rate of 0.057 m^3/min. The sour gas feed rate was 0.034 m^3/min with a H_2S concentration of 0.73 g/m^3. The superficial sour gas velocity was 0.25 cm/s. After 2–3 h, one-third of the mixed liquor was drained from the column, reducing the liquid height to 1.27 m. After a second 2-3-h operating period at this liquid height, another one-third (of the original volume) was removed, reducing the liquid level to 0.71 m. The reactor was then operated at this liquid level for another 2–3 h at the same aeration rate and sour gas feed conditions.

At the conclusion of this experiment, the mixed liquor removed from the bubble column was replaced until the reactor was half full. The bubble column was then filled to the top of the jacket (total height, 1.83 m) with fresh medium. The resulting MLSS concentration was 0.7 g/L. The above experiment was then repeated, determining

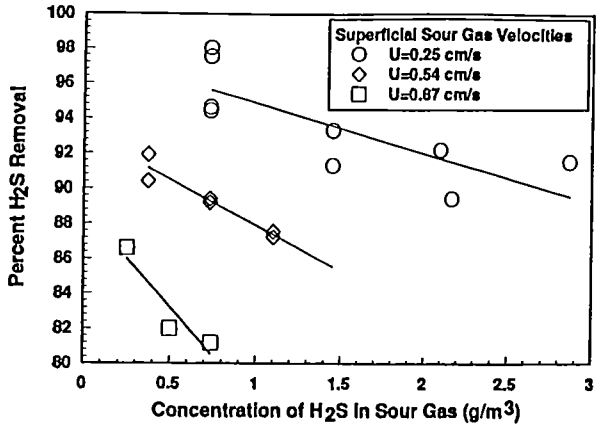

Figure 2. Removal of hydrogen sulfide (H_2S) from a sour gas in a pilot-scale bubble column: MLSS = 0.5–1.7 g/L, culture volume = 0.44 m^3, liquid height = 1.83 m, and aeration rate = 0.13 ~~$mg^3/min \cdot mL^3$~~. The superficial gas velocity for air was 0.42 cm/s. $m_g^3/min - m_l^3$

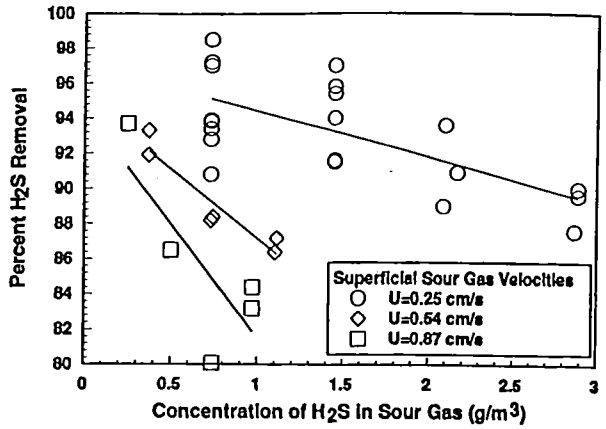

Figure 3. Removal of hydrogen sulfide (H_2S) from a sour gas in a pilot-scale bubble column: MLSS = 0.5–1.7 g/L, culture volume = 0.44 m^3, liquid height = 1.83 m, and aeration rate = 0.19 ~~$mg^3/min \cdot mL^3$~~. The superficial gas velocity for air was 0.61 cm/s. $m_g^3/min - m_l^3$

H_2S removal efficiencies at three liquid levels in the bubble column.

Analytical Experiments. Samples of mixed liquor from the column were obtained after each 8–9 h of operation of H_2S feed. MLSS was determined gravimetrically by filtering known volumes of culture medium through tared Whatman GF/C glass fiber filters (APHA, 1976). Sulfate was determined turbidometrically by precipitation with $BaCl_2$ (APHA, 1976). Elemental sulfur was determined as previously described (Sublette and Sylvester, 1987a). Hydrogen sulfide in the column outlet gas was determined every hour during operation with a H_2S feed, using GasTech (Yokohama, Japan) chromaphoric analyzer tubes with a range of 0–60 ppm (0–0.083 g/m^3). The liquid phase concentration of oxygen in the reactor was determined using a YSI polarographic electrode (Yellow Springs Instrument Co.).

Results and Discussion

Figure 2 shows the percent removal of H_2S as a function of sour gas superficial gas velocity and H_2S concentration in the sour gas at an aeration rate of 0.13 ~~$mg^3/min \cdot mL^3$~~. Hydrogen sulfide removal efficiencies were virtually identical at an aeration rate of 0.19 ~~$mg^3/min \cdot mL^3$~~ (Figure 3) and slightly improved at 0.26 ~~$mg^3/min \cdot mL^3$~~ (Figure 4). Hydrogen sulfide removal efficiency was observed to be independent of MLSS concentration; therefore, these figures contain data at both MLSS concentrations. Scatter in the data under any given set of reaction conditions was a function of the age of the culture (and increasing concentrations of waste products and cell lysis products), with the lower removal efficiencies obtained with increasing operating time. Removal efficiencies could be increased by dilution of the culture with fresh medium. Removal efficiency is seen in Figures 2–4 to decrease with increasing sour gas superficial velocity and increasing H_2S concentration in the sour gas. These reductions in removal efficiency were due to mass transfer limitations not limitations in the microbiology of the system. As noted above, elemental sulfur will accumulate in these cultures if sulfide accumulates in the bulk liquid phase. No elemental sulfur was observed during the entire course of the experiment. Increasing the flow rate of sour gas, at a constant concentration of H_2S, increased the rate of removal of H_2S from the gas. For example, at a H_2S concentration of 0.73 g/m^3, the rate of removal of H_2S was 0.10, 0.21, and 0.31 mol of $H_2S/m^3 \cdot h$ at superficial sour gas velocities of 0.25, 0.54, and 0.87 cm/s, respectively. Since k_La is a function of u_G and

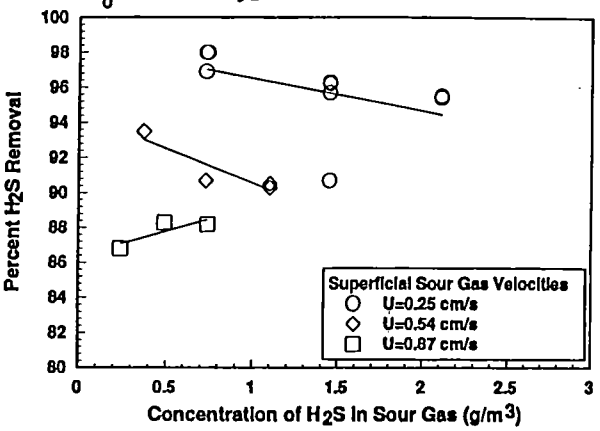

Figure 4. Removal of hydrogen sulfide (H_2S) from a sour gas in a pilot-scale bubble column: MLSS = 0.5–1.7 g/L, culture volume = 0.44 m^3, liquid height = 1.83 m, and aeration rate = 0.26 ~~$mg^3/min \cdot mL^3$~~. The superficial gas velocity for air was 0.83 cm/s. $m_g^3/min - m_l^3$

the liquid phase O_2 concentration was in excess (0.09–0.16 mM), the reaction was limited by the transfer of H_2S into the culture medium. The maximum H_2S removal rate observed in this system was 0.40 $mol/m^3 \cdot h$ at an aeration rate of 0.19 ~~$mg^3/min \cdot mL^3$~~, a sour gas superficial velocity of 0.87 cm/s, and a H_2S concentration in the sour gas of 0.97 g/m^3. $m_g^3/min - m_l^3$

As H_2S was removed from the feed gas, sulfate accumulated in the culture medium (Figure 5). The sulfate concentration was always well below inhibitory levels of 200–500 mM (Sublette, 1987). During both phases of reactor operation (before and after the addition of fresh medium), the ratio of sulfate produced to H_2S removed from the sour gas was 1.00–1.04, indicating complete oxidation of H_2S to sulfate. The MLSS concentration was seen to increase (to about 1.7 g/L) as H_2S was removed from the sour gas during each phase of operation, indicating growth of the biomass at the expense of H_2S oxidation. As H_2S was removed from the feed gas, NaOH addition was required to maintain the pH at 7.0. Overall, 1.35 equiv of OH^- was required per mole of H_2S oxidized in the column. This compares favorably with that reported for H_2S oxidation by *T. denitrificans* in bench-scale stirred-tank reactors (Sublette, 1987).

Removal efficiency increased, as expected, with increasing liquid level height and gas–liquid residence time. H_2S removal increased from 77% at a liquid height of 0.71 m to 93% at a liquid height of 1.8 m and 1.65 g/L

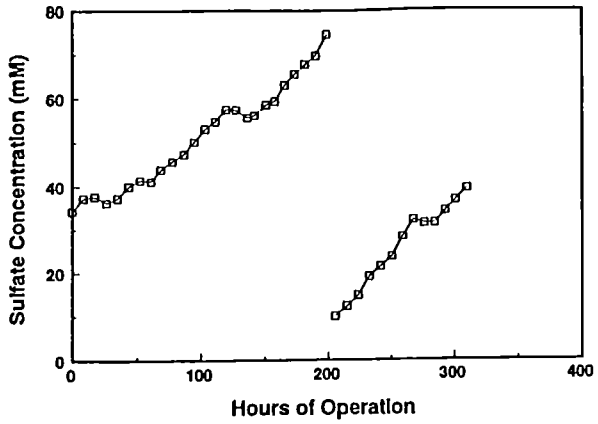

Figure 5. Sulfate accumulation in the pilot-scale bubble column receiving sour gas feeds.

MLSS. At a MLSS concentration of 0.7 g/L, H_2S removal was 86% and 97% at liquid heights of 0.71 and 1.83 m, respectively. These data suggest that increasing liquid levels above 1.8 m would result in increasingly smaller step changes in removal efficiency. As noted, removal efficiencies were greater at the lower MLSS concentration. It is likely that this effect is less a function of the MLSS concentration and more a function of the decrease in concentration (with the addition of fresh medium) of microbial waste products and products of cell lysis, which interfered with gas–liquid mass transfer.

Conclusions

A flocculated culture of *Thiobacillus denitrificans* strain F has been successfully used to remove and oxidize H_2S from a sour gas stream in a pilot-scale bubble column. Removal efficiencies exceeded 80% at sour gas superficial velocities as high as 0.87 cm/s. Limitations in H_2S removal were caused by mass transfer and not the microbiology of the system. More complete H_2S removal can be accomplished by increasing gas–liquid contact in a single reactor or using two bubble columns in series.

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