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Removal of High Concentration of H_2S in an Airlift-Loop Reactor

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A type of airlift-loop reactor inoculated with *Thiobacillus thioparus* S1 was developed for treating a gaseous stream containing high concentrations of hydrogen sulfide. This result showed superior performance of the bioreactor for H_2S removal. The bioreactor systems allowed an efficiency of 99 % when fed with 380-5400 ppmv H_2S. And the maximum elimination capacity was about 235 g-H_2S m^{-3} h^{-1}. At high inlet concentration of 5120 ppmv, the conversion products were mainly sulfur and the production rate of SO_4^{2-} was only 2.8 mg h^{-1}. The biokinetic constants, V_m and K_s for the airlift-loop bioreactor were 277.8 g-H_2S m^{-3} h^{-1} and 366.3 ppmv, respectively.

Key Words: Biological deodorization, *Thiobacillus thioparus*, Airlift-loop reactor, Hydrogen sulfide.

INTRODUCTION

The emission of sulfur-containing compounds is found in many industrial activities such as petroleum refining, pulp and paper manufacturing, livestock poultry raising and food processing[1]. Among these sulfur compounds, hydrogen sulfide (H_2S), is a highly toxic and corrosive gas, can be the standard indicator among the obnoxious odors and therefore the amount released into the air is required to be regulated strictly[2]. Physico-chemical methods tend to be costly and are associated with their own pollution problems. As a result, biological treatment methods have been proposed as a convenient alternative.

Three major types of bioreactor that currently dominate waste gas biotreatment are bioscrubbers, biofilters and biotrickling filters[3]. Over the years, several methods have been used in removal of H_2S for achieving a better performance of biodesulfurization systems. Nevertheless, the development of new bioreactors has rarely been reported in recent years. In comparison, air-lift reactors have outstanding advantages: a simple construction, an excellent heat transfer capacity, a reasonable interphase mass transfer rate and good mixing properties at low energy consumption[4]. Several papers published by Janssen and co-workers have described one process using airlift-loop reactor for gas desulfurization[5,6]. However, relevant differences in the present manuscript are (1) a simplified process is presented for gas desulfurization and H_2S-containing gas is directly contacted with bacteria in one airlift-loop bioreactor, (2) the use of a different micro-organism and (3) neutral conditions of operation instead of natron-alkaliphilic ones. On the other hand, air-lift reactors are used in a variety of biotechnological processes and have shown good performance[4,7-9].

In this study, *T. thioparus* S1 isolated in our laboratory was used for removal of H_2S. Because this bacteria can oxidize high concentrations of H_2S, have a short acclimation period and the optimal pH is neutral and therefore the hydrogen sulfide solubility will be greater. The main purpose of this work is to study the feasibility of treating air contaminated with H_2S using a bench-scale airlift-loop reactor inoculated with pure culture (*T. thioparus* S1) and to find the optimum conditions for an efficient H_2S-removal in an airlift-loop bioreactor. Besides, metabolic product and kinetic analysis of the biodesulfuration were also investigated.

EXPERIMENTAL

T. thioparus S1 was isolated from a hot spring in Sichuan province and used in this study. The mineral salts medium (Starkey) described by Vishniac[10] was used for periodic maintenance and production of cells.

General procedure: Fig. 1 presents the experimental set-up, in which the airlift-loop reactor was built using a PVC column (40 mm i.d. × 400 mm) and an internal column (20 mm i.d. × 200 mm). The original liquid composition in the airlift-loop reactor was a mixture of Starkey medium (without sodium thiosulfate) and the inoculum (10 %, v/v). The total liquid volume after inoculation was 350 mL at 30 ºC. Air was supplied with an air compressor (ACO-007, China) through a filter and measured by a gas flow meter. H_2S was introduced by passing the air stream over an H_2SO_4 solution into which a

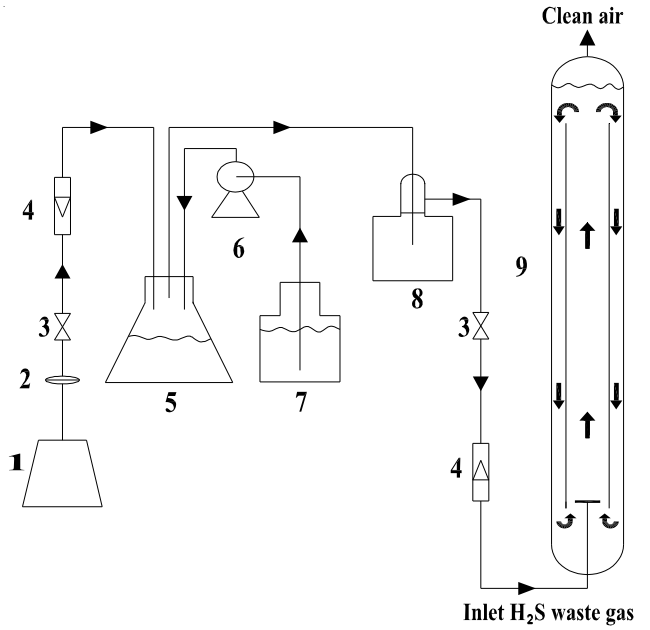

Fig. 1. Schematic diagram of the airlift-loop bioreactor system 1 air compressor; 2 air filter; 3 on-off valve; 4 flow meter; 5 H_2SO_4 tank; 6 pump; 7 Na_2S tank; 8 expansion tank; 9 airlift-loop reactor

solution of Na_2S was dripped. Gas phase H_2S concentrations ranging from 380-9000 ppmv were obtained by changing the Na_2S concentration and/or dripping rate. During reactor operation, the experimental temperature was controlled at 30 ºC and the pH value was adjusted to 7.5, unless otherwise indicated.

Detection methods: Inlet H_2S gas concentrations (below 5000 ppmv) in the reactor were periodically measured by gas detector tubes (Yudong, China) in the range of 200-5000 ppmv and higher concentrations (above 5000 ppmv) were measured by titration using an iodometric method (GB/T 11060.1-1998, Chinese standard method). Outlet concentrations were periodically measured by gas detector tubes (Gastec 4HM, Japan) in the range of 25-1600 ppmv. The cell numbers in the bioreactor were determined by the use of a haemacytometer (7103-s, China) under an optical microscope (Nikon Eclipse E100). Sulfate analysis was carried out photometrically by a turbidimetric method (GB 6911.2-86, Chinese standard method), which was performed by measuring the absorbance on a spectrophotometer (Mapada, UV-1800PC). The pH was determined using a pH meter (pHS-25, China).

RESULTS AND DISCUSSION

Performance of the airlift-loop bioreactor: When the system operated at pseudo steady state, at which growth of the cells terminated resulting in the growth maximum of approximately 4.5×10^8 cells mL^{-1}, different inlet H_2S concentration (in the range from 380-9000 ppmv) and the retention time (in the range from 70 -210 s) were introduced into the bioreactor to test the H_2S removal performance of the system. Fig. 2 shows the removal efficiencies (RE) as a function of the H_2S concentration and of the retention time. The decline in removal efficiency as the retention time decreases was due to an insufficient contact time between H_2S and the biomass. A gradual decrease in efficiency as the gas concentration

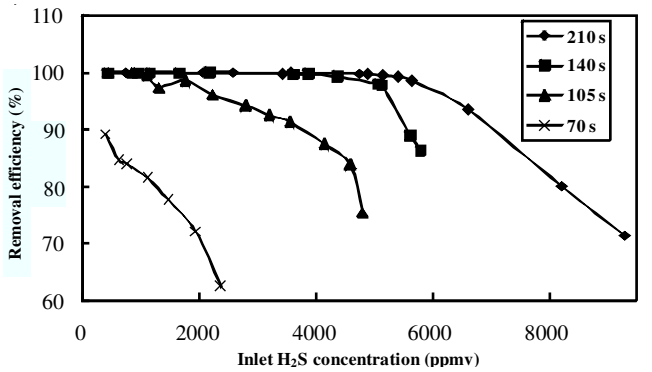

Fig. 2. H_2S removal efficiency *versus* inlet concentration at different retention time

increases was thought to be a problem related to gas diffusion and the low solubility of H_2S in the liquid phase. Therefore, the bioreactor reached an efficiency of 99 % when fed with 5400 ppmv of H_2S at rentention time of 210 s or 4400 ppmv of H_2S at rentention time of 140 s.

The relationship between the inlet loading (L_{in}) and the elimination capacity (EC) for hydrogen sulfide is shown in Fig. 3. The increase in the elimination capacity at retention time of 140 s was marked and the maximum elimination capacity was approximately 235 g-H_2S m^{-3} h^{-1} (removal efficiency of 97.8 %). This capacity is high in comparison with other studies on bioreactor of H_2S carried out with other neutrophilic thiobacilli. Thus, the airlift-loop bioreactor inoculated with *T. thioparus* S1 can reduce its working volume or treat high inlet H_2S loading better than other biosystems.

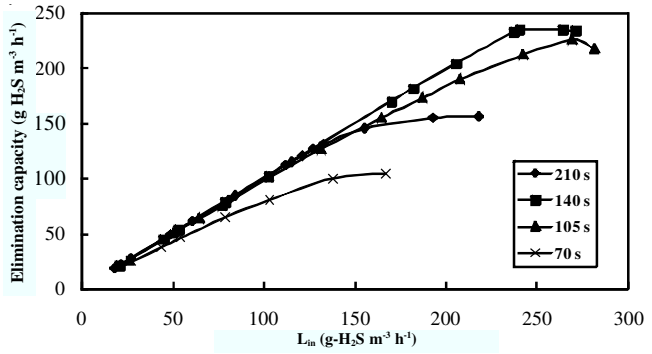

Fig. 3. H_2S elimination capacity *versus* inlet loading at different retention time

Hydrogen sulfide is used as electron donor by the sulfur oxidizing bacteria. The oxidation of H_2S occurs in stages and the first oxidation step results in the formation of elemental sulfur, S^0. When the supply of H_2S has been depleted, additional energy can be obtained from the oxidation of sulfur to sulfate. As shown in Table-1, the sulphur content in the sulphates was declined gradually as the inlet concentration increases. At a inlet concentration of 5120 ppmv, the conversion products were mainly sulfur and the production rate of SO_4^{2-} was 2.8 mg h^{-1}. But a sharp decrease of the removal efficiency was observed with a high level of inlet concentration (5780 ppmv). This may be due to G-L mass transfer restrictions. Under oxygen-limiting conditions, *i.e.*, gas flow rate is low, elemental sulfur is the major end product of the sulfide oxidation[11]. On the other hand, sulfate is formed under circumstance of sulfide limitation (Table-2).

TABLE-1
AMOUNT OF SO_4^{2-} FORMED AT DIFFERENT H_2S INLET CONCENTRATION*

C_{in} (ppmv)	RE (%)	Production rate of SO_4^{2-} (mg h^{-1})
2186	99.5	1.1
3881	99.7	0.8
4385	99.1	2.0
5120	97.8	2.8
5780	90.2	10.6

*At a constant H_2S retention time of 140 s.

TABLE-2
AAMOUNT OF SO_4^{2-} FORMED AT DIFFERENT GAS FLOW RATES*

Gas flow rate (L h^{-1})	RE (%)	Production rate of SO_4^{2-} (mg h^{-1})
6	99.9	0.1
12	99.5	1.1
15	98.4	3.8
18	86.5	36.2

*At H_2S inlet concentration of 2150 ± 50 ppmv.

Continuous operation of the bioreactor: It is necessary to examine the removal efficiencies and characteristics of a continuous treatment by the airlift-loop bioreactor. An experiment was performed at a constant retention time of 140 s. The removal efficiencies for H_2S in the airlift bioreactor during 19 days of operation are indicated in Fig. 4. The initial biomass concentration was 0.6×10^8 cells mL^{-1}, with a growth maximum of 4.54×10^8 cells mL^{-1} after a 4 d acclimation period. A short acclimation period showed that the microorganism had good adaptive ability to remove H_2S as a source of energy. More than 97 % H_2S removal was achieved 4 days later due to effective biological oxidation. To evaluate the adaptability of the *T. thioparus* airlift bioreactor to upset conditions, the H_2S gas supplied was suddenly increased from 2700-4000 ppmv on the 4th day and allowed to continue for 24 h, later the concentration was brought down to original level of 3000 ppmv. The removal efficiency was slightly affected by the shock loading, which was constant through out the period of operation. This result showed superior performance of the bioreactor for H_2S removal during the accidental shock loading operation. Some temporary decreases of the removal efficiency were observed after 19 days, mostly due to decrease of the cell numbers and accumulation of SO_4^{2-}.

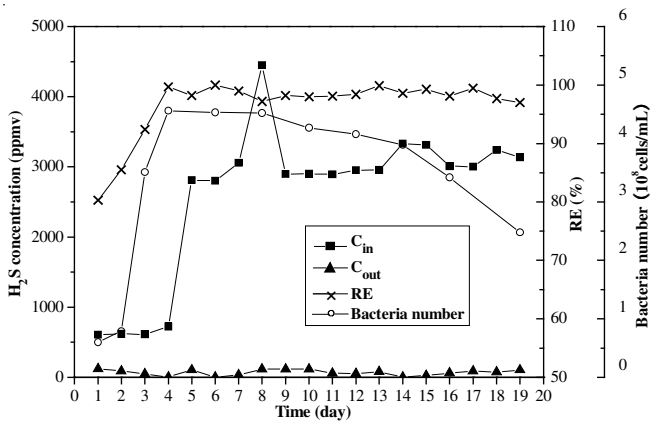

Fig. 4. Performance of the airlift-loop bioreactor during 19 day operation

Kinetic studies: During the removal of H_2S in the airlift-loop bioreactor, pollutants are transferred from the gas phase to the liquid and undergo aerobic biological degradation. Generally, internal and external diffusion effect on overall rate could be neglected and the product inhibition does not exist in the biodesulfuration process. The removal rate of H_2S in the bioreactor was modeled using a modified Michaelis-Menten type model[12]:

$$\frac{1}{R} = \frac{K_s}{V_m}\frac{1}{C_{ln}} + \frac{1}{V_m} \quad (1)$$

where $R = [(C_{in} - C_{out}) \times F_g/V \times \beta]$ (g-H_2S m^{-3} h^{-1}) is apparent removal rate; V_m (g-H_2S m^{-3} h^{-1}) is the maximum elimination rate; K_s (ppmv) is the apparent half-saturation constant; $C_{ln} = [C_{in} - C_{out})/\ln (C_{in}/C_{out})]$ (ppmv) is logarithmic mean concentration; C_{in} (ppmv) is the inlet H_2S concentration; C_{out} (ppmv) is the outlet H_2S concentration; $\beta = [(M \times 10^{-3})/[22.4 \times (273 + T)/273]]$ is a conversion factor; M is the pollutant molecular weight and T the operating temperature (ºC).

Multiplication by C_{ln}:

$$\frac{C_{ln}}{R} = \frac{1}{V_m}C_{ln} + \frac{K_s}{V_m} \quad (2)$$

Fig. 5 presents the linear relation of (C_{ln}/R) *versus* (C_{ln}) corresponding to eqn. 2. A good linear regression coefficient of 0.987 between experimental data points and the predicted curves was found. The maximum elimination rate (V_m) was 277.8 g-H_2S m^{-3} h^{-1} and the apparent half-saturation constant (K_s) was 366.3 ppmv.

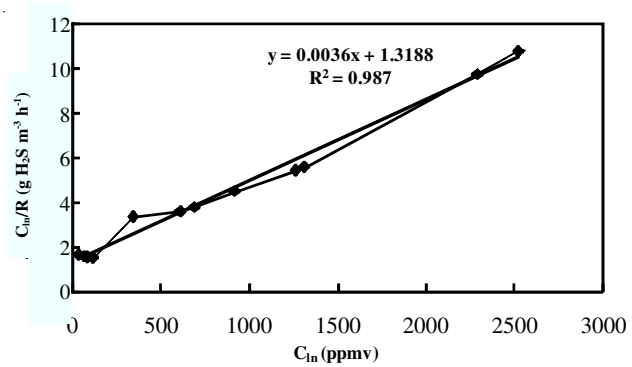

Fig. 5. Linear relationship between C_{ln}/R and C_{ln} in the airlift-loop bioreactor

Conclusion

Airlift-loop bioreactor had significant potential to treat H_2S odor gas, which achieved an average 97.8 % removal efficiency of H_2S at the inlet H_2S concentration of 5120 ppmv. The maximum elimination capacity was 235 g-H_2S m^{-3} h^{-1}. The performance can be modeled by a Michaelis-Menten equation. The maximum removal rate and the apparent half-saturation constant were found to be 277.8 g-H_2S m^{-3} h^{-1} and 366.3 ppmv, respectively.

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REFERENCES

1. M. Ramírez, J.M. Gómez, G. Aroca and D. Cantero, *Bioresour. Tech.*, **100**, 4989 (2009).
2. P. Oyarzún, F. Arancibia, C. Canales and G.E. Aroca, *Process Biochem.*, **39**, 165 (2003).
3. G.R. Moosavi, A.R. Mesdaghinia, K. Naddafi, F. Vaezi and R. Nabizadeh, *J. Biol. Sci.*, **5**, 170 (2005).
4. S.Y. Chen and J.G. Lin, *Water Res.*, **38**, 3205 (2004).
5. P.L.F. van den Bosch, M. de Graaff, M. Fortuny-Picornell, R.C. van Leeradm and A.J.H. Janssen, *Appl. Microbiol. Biot.*, **83**, 579 (2009).
6. P.L.F. van den Bosch, O.C. van Beusekom, C.J.N. Buisman and A.J.H. Janssen, *Biotech. Bioeng.*, **97**, 1053 (2007).
7. M.R. Mehrnia, J. Towfighi, B. Bonakdarpour and M.M. Akbarnejad, *Biochem. Eng. J.*, **22**, 105 (2005).
8. H. Nikakhtari and G.A. Hill, *J. Chem. Tech. Biot.*, **81**, 1029 (2006).
9. D. Park, D.S. Lee, J.Y. Joung and J.M. Park, *Process Biochem.*, **40**, 1461 (2005).
10. Wolf Vishniac, *J. Bacteriol.*, **64**, 363 (1952).
11. H. Duan, R. Yan and L.C.C. Koe, *Appl. Microbiol. Biot.*, **69**, 350 (2005).
12. M. Hirai, M. Ohtake and M. Shoda, *J. Ferment. Bioeng.*, **70**, 334 (1990).