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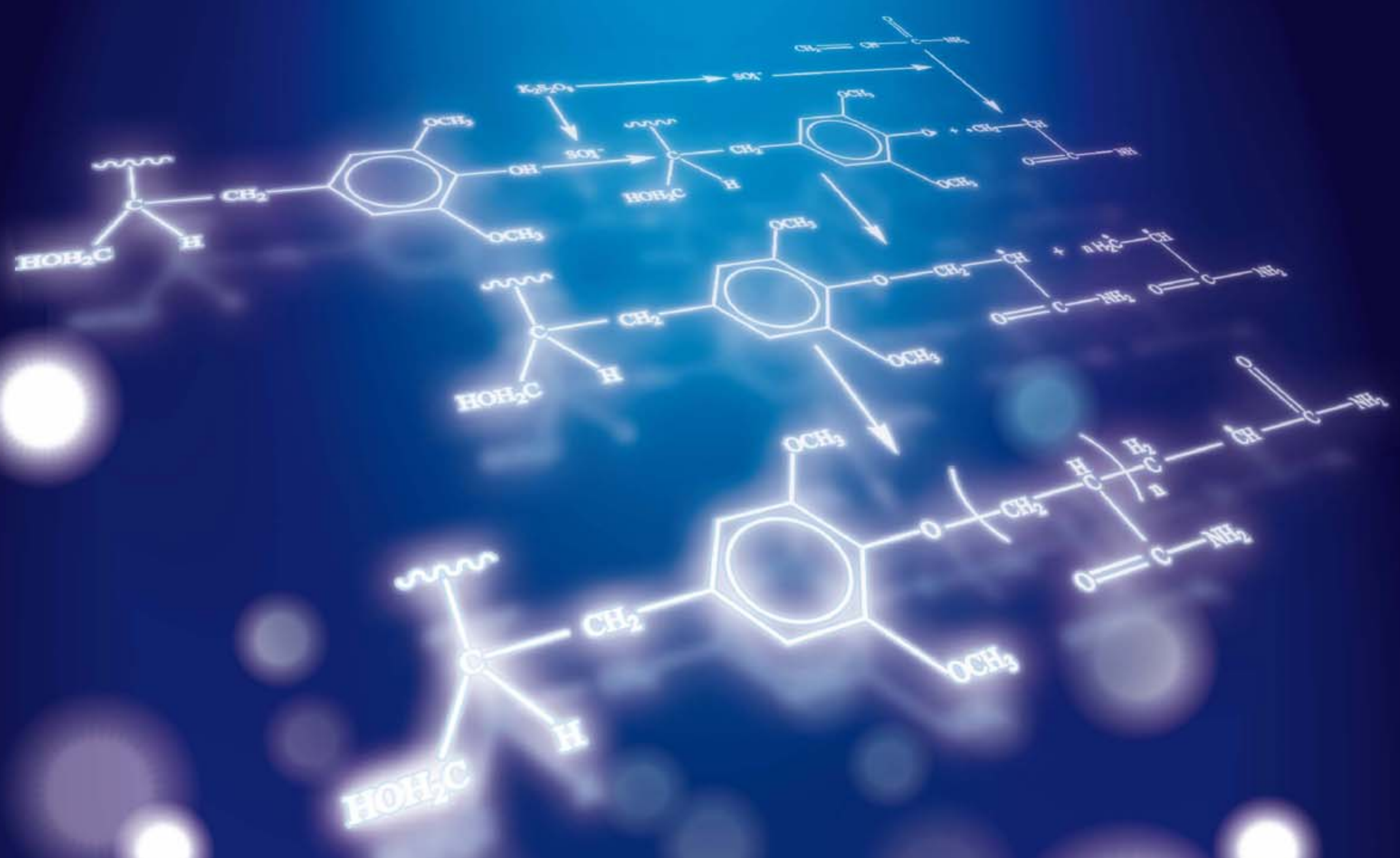

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Effect of operating parameters on sulfide biotransformation to sulfur

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Abstract

A laboratory-scale bioreactor with polyethylene semi-soft packing was constructed and utilized to determine the efficiency of sulfide biotransformation to sulfur under various operating parameters. Sodium sulfide dissolved in tap water was pumped into the bioreactor as sulfide for biological desulfurization. The sulfide, sulfur and sulfate-S in the effluent and the sulfide purged as gas-phase H_2S were determined to investigate the effects of operating parameters, such as pH, DO, hydraulic retention time (HRT), temperature and salinity, on the sulfide oxidation products. The activity of bacteria was highest at pH 7.8–8.2. The maximal sulfide removal load was 7.25 kg/(m^3·day), with a 322.07 mg/L influent sulfide concentration and 4.80 mg/L DO. The increase of DO value corresponds to a decrease in the sulfur yield. The reactor had the highest sulfide removal load and sulfur yield at 2.55 mg/L DO. HRT had little effect on desulfurization efficiency when the sulfide removal load was kept constant. The most effective desulfurization temperature was 33°C. The sulfide removal load decreased from 2.85 to 0.51 kg/(m^3·day) with increasing salinity from 0.5% to 2.5% (*m/m*).

Key words: sulfide; sulfur; biotransformation; operating parameters

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Introduction

Sulfide is emitted into the environment as dissolved sulfide in wastewater and as H_2S gas. Sulfide-containing wastewaters are produced by a number of industrial activities, such as petrochemical plants, oil refining plants, chemical fertilizer plants, synthetic fiber plants, and tanneries (Janssen et al., 1999). Sulfide emission is a major problem associated with the anaerobic treatment of sulfate- and sulfite-containing wastewaters (Buisman and Lettings, 1990; Fox and Venkatasubbiah, 1996). In addition, many investigations have reported that the H_2S concentration in biogas was as high as 5000 ppm (Namgung et al., 2012). Biogas can provide a clean, easily-controlled source of renewable energy from organic waste materials for a small labor input, replacing firewood or fossil fuels. All over the world, especially in China, governments have also invested heavily in the construction of biogas engineering facilities. Sulfide can cause facility corrosion, unnecessary production of byproducts, and possible public exposure as well as the resultant health issues (Liao et al., 2008). The removal of sulfide in the wastewater and gases is therefore essential. Sulfide removal methods commonly include physical, chemical and biological processes (Buisman et al., 1990). The following reactions occur in the biological desulfurization of sulfide wastewater (Buisman et al., 1989):

$$2HS^- + O_2 \longrightarrow 2S^0 + 2OH^- \quad (1)$$

$$2S^0 + 3O_2 \longrightarrow 2SO_4^{2-} + 2H^+ \quad (2)$$

H_2S is first absorbed in the solution by the wet scrubber (absorption tower reaction, as shown in Reaction (3)) before using biological desulfurization to treat H_2S in the emitted gases.

$$H_2S(g) + OH^- \Longleftrightarrow HS^-(L) + H_2O \quad (3)$$

The feasibility of biological desulfurization mainly depends on the sulfide conversion rate and the efficiency of converting sulfide into sulfur. If sulfide is oxidized to sulfur and hydroxide, the generated hydroxide may be used to absorb H_2S in the treated gases. Compared with chemical desulfurization, the biological approach consumes smaller quantities of chemicals. Biological desulfurization has the advantages of low operating costs and minimal generation of undesirable byproducts. An increasing number of researchers have recently turned their attention to biological desulfurization technology (Gao et al., 2011; Mahmood et al., 2008; Henshaw and Zhu, 2001; Nishimura and Yoda, 1997).

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In this study, a bioreactor with semi-soft packing was constructed to develop an effective, low-cost, and rapid biotechnological process for sulfide removal in which sulfide is converted into elemental sulfur. The operating parameters, including pH, dissolved oxygen (DO), hydraulic detention time (HRT), temperature and salinity were optimized in the bioreactor with simulated wastewa er.

1 Materials and methods

1.1 Experimental setup and operating conditions

This study was carried out in a laboratory-scale bioreactor comprised of a Plexiglas column (800 mm in height and 80 mm in diameter) (**Fig. 1**). Polyethylene semi-soft packing was packed in the bioreactor as a carrier for microbial growth. The sulfide-oxidizing bacteria were obtained from municipal sludge acclimation. Sodium sulfide was dissolved in the tap water as the sulfide for biological desulfurization. Nutrient salt (the weight ratio of KH_2PO_4:$MgSO_4$:urea = 80:50:36) was also added to the sodium sulfide solution. The mixed solution was continuously pumped into the bioreactor. The HRT of the bioreactor was 30 min except for the experiments on HRT operating conditions. Hydroxyl was generated by the hydrolysis of sodium sulfide and the conversion of sulfide to elemental sulfur. To adjust the solution pH, 0.5% HCl solution was pumped into the bioreactor. The oxygen concentration in the solution was controlled by an air compressor and air mass meter. H_2S escaping from the solution was absorbed by a 10% sodium hydroxide solution and determined by an iodometric method.

1.2 Analysis methods

The sulfide in the solution was determined by an iodometric method. Elemental sulfur was measured by liquid-liquid extraction coupled with gas chromatography-mass spectroscopy (GC-MS) (Liu et al., 2012). The extraction solvent was CS_2. A GC (Agilent 7890A, USA)-MS (Agilent 5975C) instrument was equipped with a HP5-MS column (30 m × 0.25 mm × 0.25 μm). The GC column was held at 40°C for 2 min; ramped at 50°C/min to 200°C, 6°C/min to 240°C, 50°C/min to 290°C; and held for 5 min. The solvent delay was 3.5 min. Sulfate was determined by ion chromatography (Dionex ICS-1000, USA). IonPac AS23 (4 mm × 250 mm) was selected as the separation column. The column temperature was 30°C. A solution of 4.5 mmol Na_2CO_3 and 0.8 mmol $NaHCO_3$ was used as the eluent with a flow rate of 1.0 mL/min. The influent volume was 25 μL. Sulfate is reported as sulfur equivalents, in units of (mg S as species)/L (Henshaw et al., 1998). The DO, pH, salinity were measured by a multi-parameter water quality analyzer (WTW 340i, Germany).

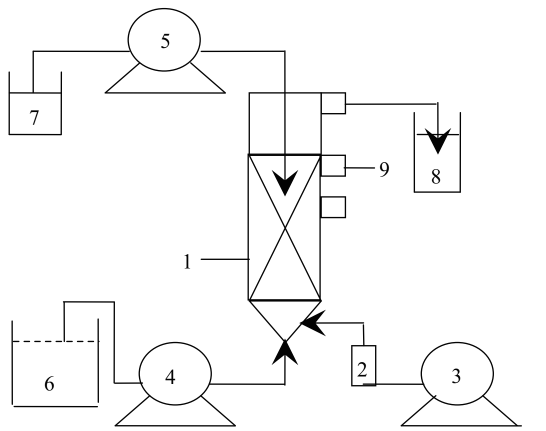

Fig. 1 Flow chart of the experiment. (1) bioreactor; (2) air mass meter; (3) air compressor; (4), (5) peristaltic pump; (6) sodium sulfide wastewater; (7) 0.5% HCl solution; (8) 10% sodium hydroxide solution; (9) sampling port.

2 Results and discussion

2.1 Effect of pH on biological desulfurization efficiency

The pH of the solution not only affects the activity of bacteria, but also determines the sulfide morphology. The effect of pH on the desulfurization was investigated. The experiment was run for three days for each pH condition before the data collection. The experimental data are shown in **Fig. 2** for influent sulfide concentrations of 120–130 mg/L and a dissolved oxygen concentration of 2 mg/L. The concentration of sulfide purged as H_2S increased from

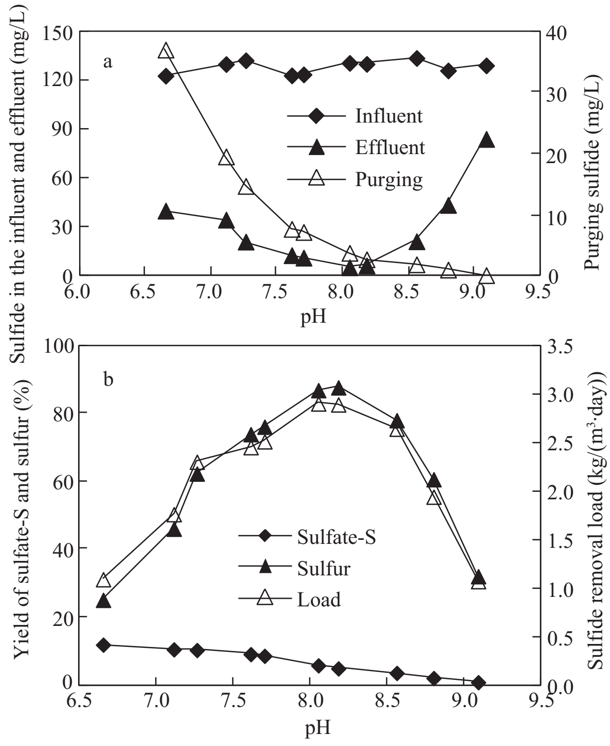

Fig. 2 Effect of pH on the sulfide morphology in the biological desulfurization process (a) and the yield of sulfate-S and sulfur as well as the sulfide removal load (b).

0.27 to 37.01 mg/L as the pH of the solution decreased from 9.09 to 6.65. The bacterial activity was highest at pH 7.8–8.2 with 6 mg/L sulfide in the effluent. The maximal sulfide removal load was 2.90 kg/(m^3·day), and the conversion efficiency of sulfide to sulfur was 87.60%. With the increase of pH from 6.65 to 9.07, the yield of sulfate-S decreased from 11.89% to 0.84%.

2.2 Effect of DO on biological desulfurization efficiency

Unlike activated sludge processes, a higher DO concentration is beneficial for oxygen transfer to the biofilm inner surface in contact oxidation processes. A high concentration of DO may increase the sulfide removal load of the reactor on one hand, but may result in sulfur oxidation to sulfate on the other hand. Two series of experiments were conducted to investigate the effect of DO on desulfurization efficiency at pH 7.8–8.2. Some of the experiments were run under the condition of almost the same sulfide concentration but different DO values. In the rest of the experiments, the influent sulfide concentration was increased with increasing DO. The experimental data are shown in **Fig. 3a** for approximately 80 mg/L sulfide in the influent. When the DO was increased from 0.55 to 2.55 mg/L, the sulfide concentration in the effluent decreased from 60.25 to 6.67 mg/L. When the DO was further increased to 7.21 mg/L, sulfide in the effluent was still approximately 6 mg/L. The yield of sulfur decreased from 87.08% to 65.83%, and the yield of sulfate-S increased from 4.95% to 26.72% as the DO increased from 2.55 to 7.21 mg/L.

In another series of experiments, the sulfide in the influent increased from 90.05 to 363.02 mg/L and the sulfide in the effluent increased from 5.70 to 57.72 mg/L as the DO increased from 1.10 to 5.70 mg/L, as shown in **Fig. 3b**. The sulfide in the influent increased from 322.07 to 363.02 mg/L, and the sulfide in the effluent increased from 19.97 to 57.72 mg/L as the DO increased from 4.80 to 5.70 mg/L. The sulfide removal load was highest (7.25 kg/(m^3·day)) for 322.07 mg/L sulfide and 4.80 mg/L DO. The yield of sulfur decreased from 92.20% to 64.70% and the yield of sulfate-S increased from 1.10% to 17.50% at the above experimental conditions.

2.3 Effect of hydraulic retention time on biological desulfurization efficiency

The sulfide concentration fluctuates for sulfide-containing wastewater and gases. The maximal sulfide removal load depends on the characteristics of the biological reactor. HRT is an operating parameter that can be adjusted to change the sulfide concentration. In the experiment shown in **Table 1**, the sulfide removal load was kept constant, and the sulfide concentration in the influent was changed throughout the experiment. With influent sulfide concentration increased from 63.83 to 209.06 mg/L and the HRT increased from 15 to 60 min, the effluent sulfide concentration increased from 10.23 to 15.83 mg/L. The yield of sulfur and sulfate-S was 74.49%–78.20% and 9.53%–14.54%. A longer HRT resulted in a slight increase in the yield of sulfate-S.

2.4 Effect of temperature on biological desulfurization efficiency

The solution temperature was set at 15, 25, 33, and 45°C to investigate the effect of temperature on bacterial

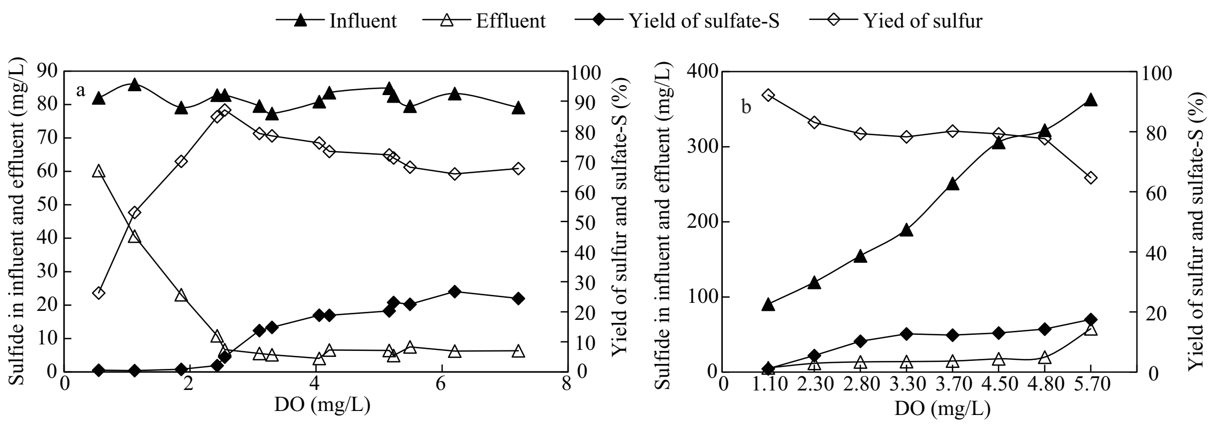

Fig. 3 Effect of DO on desulfurization efficiency with identical influent sulfide concentration (a), and the increasing influent sulfide concentration and increasing DO (b).

Table 1 Effect of HRT on desulfurization

HRT (min)	Sulfide in influent (mg/L)	Load (kg/(m^3·day))	Sulfide in effluent (mg/L)	Yield of sulfur (%)	Yield of sulfate-S (%)
15	63.83	4.95	10.23	74.49	9.53
22	85.81	4.64	12.42	75.57	9.98
30	114.42	4.99	12.55	78.20	10.87
45	165.04	4.69	14.76	77.91	13.18
60	209.06	4.60	15.83	77.90	14.54

Table 2 Effect of temperature on desulfurization

Temperature (°C)	Sulfide (mg/L)			Load (kg/(m^3·day))	Yield of sulfur (%)	Yield of sulfate-S (%)
	Influent	Effluent	Purging			
15	201.81	53.22	0.92	3.55	71.23	1.42
25	198.58	27.41	1.71	4.09	83.12	1.44
33	202.56	14.25	2.14	4.51	89.37	1.65
45	197.02	12.84	3.64	4.42	80.65	9.24

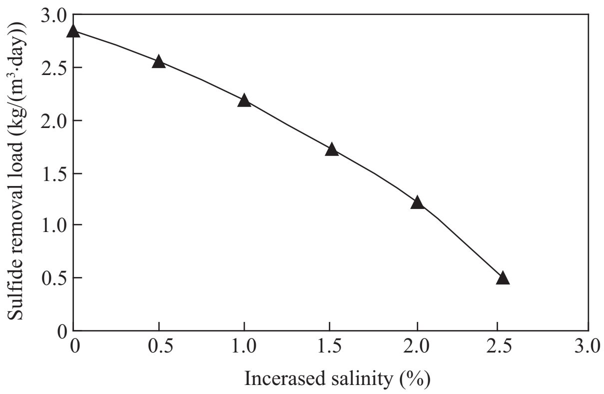

Fig. 4 Effect of increased salinity on sulfide removal load.

activity under the condition of pH 7.8–8.2 and 2.0–2.5 mg/L DO. The experimental results are shown in **Table 2**. The influent sulfide concentration was approximately 200 mg/L. When the solution temperature was gradually increased from 15 to 45°C, the effluent sulfide concentration decreased from 53.22 to 12.84 mg/L and the concentration of sulfide purged rose from 0.92 to 3.64 mg/L. The sulfide removal load and yield of sulfur decreased slightly with increasing solution temperature from 33 to 45°C. The yield of sulfate-S was gradually increased at higher solution temperature. Based on the above experiments, the most effective desulfurization temperature was 33°C.

2.5 Effect of salinity on biological desulfurization efficiency

The absorption liquid is recycled to reduce operation costs when biological desulfurization technology is applied to treat hydrogen sulfide-containing gases. Increasing the salinity of the absorption liquid creates a hypertonic environment, leading the water in the bacteria to diffuse out. Because of the loss of water, the bacteria will shrivel up and eventually die. Salinity is an important operating parameter for biological desulfurization systems. To investigate the effect of salinity on sulfide removal load, sodium sulfate was added to a sodium sulfide solution to simulate a high-salinity absorbing liquid. Concentrations of sodium sulfate were 0.5%, 1.0%, 1.5%, 2.0% and 2.5% (*m/m*). The experiment was run for three weeks for each salinity condition before the data was recorded. In the experiment shown in **Fig. 4**, the sulfide removal load decreased from 2.85 to 0.51 kg/(m^3·day) with increasing salinity.

3 Conclusions

The bacterial activity was highest at pH 7.8–8.2. Increasing the DO decreased the yield of sulfur. The reactor had the highest sulfide removal load and yield of sulfur at 2.55 mg/L DO. The HRT had little effect on the desulfurization efficiency when the sulfide removal load was kept constant. The most effective desulfurization temperature was 33°C. The sulfide removal load decreased from 2.85 to 0.51 kg/(m^3·day) with increasing salinity from 0.5% to 2.5% (*m/m*). It was necessary to keep an appropriate salinity in the reactor based on the desulfurization load.

Acknowledgments

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