

BIODESULFURIZATION OF FLUE GASES USING SYNTHESIS GAS DELIVERED AS MICROBUBBLES

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Keywords: Biodesulfurization, synthesis gas, microbubbles

Introduction

Anaerobic treatment processes for biodegradation of hazardous materials have increasingly been gaining attention in environmental applications. Microbial processes utilizing sulfate reducing bacteria (SRB), in particular, have found potential applications in variety of treatment processes such as flue gas desulfurization [1,2], gypsum reclamation [3], sulfur recovery from sulfite/sulfate wastewater from pulp and paper, chemical and mining industries [4], and degrading explosive materials [5]. However, in all these applications, the source of electron donor is a major factor on the economics of the process. Previously, we have proposed a microbial process with sewage digest as an attractive low-cost feedstock for SRB cultures in the desulfurization of flue gases and sulfite/sulfate-laden industrial waste water [6]. In that process, a columnar reactor with mixed SRB cultures immobilized in BIO-SEP™ polymeric porous beads with sewage digest as a carbon and energy source exhibited conversion rate of 16.5 mmol sulfite/h•L (32 kg/d•m³) with 100% conversion to H₂S. Though municipal sewage digest is a readily available low-cost carbon source, the real cost of the medium depends on the location of the sewage treatment plant and power plant and on the transportation involved in bringing the sewage back and forth from the sewage plant. Therefore, the current research has been focused on an alternative low-cost feedstock. Various groups have demonstrated that SRB could be supported by carbon dioxide and/or carbon monoxide as the sole carbon source and hydrogen as the energy source [7-11]. Du Preez et al. [8,10] operated a sulfate-reducing reactor with a mixed SRB population to demonstrate the feasibility of using syn-gas as the feed source for SRB. Recently, van Houten et al. [9] reported the operation of a gas-lift sulfate-reducing reactor that was fed a CO-H₂ mixture (up to 20% CO) and yielded a maximum sulfate conversion rate of 30 g SO₄²⁻/d•L.

In our study, we have focused our research on utilizing gas mixture containing 36% H₂, 47% CO, 10% CO₂, 5% CH₄ and balance N₂ as a model coal synthesis gas as a low-cost feedstock. This composition is typical of an oxygen blown, coal fed gasifier. Coal synthesis gas will be readily available in power plants and the biological utilization of syn-gas as a carbon and energy source produces no organic end product that has to be processed prior to its disposal. Coal synthesis gas is, however, sparingly soluble in aqueous phase. Our process utilizing SRB with syn-gas feedstock may be mass transfer limited and methods to enhance the mass transport have been investigated. A CSTR with cell recycle and a trickle bed reactor with cells immobilized in BIO-SEP™ polymeric beads were operated with syn-gas feedstock to obtain maximum productivity for SO₂ reduction to H₂S. The CSTR reactor was then fed with syn-gas as microbubbles in an effort to improve the mass transfer properties.

Materials and Methods

Microbial Culture and Media

Mixed SRB cultures were originally isolated from sewage solids obtained from the DAF unit of a municipal sewage treatment plant at Oak Ridge, TN. The cultures were grown in lactic acid media (LA) which consists of 3.6 g/L citric acid, 0.8 g/L CaCl₂, 1.0 g/L NH₄Cl, 0.5 g/L K₂HPO₄, 1.0 g/L yeast extract, 0.52 g/L FeCl₂, 5.8 mL/L of sodium lactate (60% syrup), 0.518 mL/L butyric acid, and 0.05 g/L cysteine HCL. A minimal salts media (MS) was also used; 1.2 g/L Na₂HPO₄, 1.8 g/L KH₂PO₄, 0.7 g/L MgCl₂, 0.2 g/L NH₄Cl, 0.04 g/L FeCl₃, 50 mL/L mineral water, 0.2 mL/L Batch vitamin solution, and 15 mL/L heavy metal solution (HMS). The Batch vitamin solution contains the following: 2.0 mg/L biotin, 2.0 mg/L folic acid, 10.0 mg/L pyridoxine hydrochloride, 5.0 mg/L thiamine

hydrochloride, 5.0 mg/L riboflavin, 5.0 mg/L nicotinic acid, 5.0 mg/L DL-calcium pantothenate, 0.1 mg/L vitamin B-12, 5.0 mg/L p-amino benzoic acid, and 5.0 mg/L lipoic acid. The HMS solution contains the following: 1.5 g/L EDTA, 0.1 g/L $ZnSO_4 \cdot 7H_2O$ and 6 mL/L of a trace element solution (0.0507 g/L $AlCl_3$, 0.139 g/L KI, 0.139 g/L KBr, 0.139 g/L LiCl, 3.060 g/L H_3BO_3 , 0.280 g/L $ZnCl_2$, 0.326 g/L $CuCl_2 \cdot 2H_2O$, 0.513 g/L $NiCl_2 \cdot 6H_2O$, 0.513 g/L $CoCl_2 \cdot 6H_2O$, 0.139 g/L $SnCl_2 \cdot 2H_2O$, 0.163 g/L $BaCl_2 \cdot 2H_2O$, 0.139 g/L $Na_2MoO_4 \cdot 2H_2O$, 0.139 g/L $CuSeO_4 \cdot 5H_2O$, and 0.024 g/L $NaVO_3$).

In serum bottles, the sulfate source was provided by the addition of up to 4.0 g/L of Na_2SO_4 or $MgSO_4$. In the reactors, the sulfite source was provided by a gas mixture containing 5% SO_2 , 5% CO_2 , and balance N_2 . For growth on synthesis gas, a mixture of 47% CO, 36% H_2 , 10% CO_2 , 5% CH_4 , and the balance N_2 was used. For serum bottle studies, 100 mL of MS media was put into a ~150 mL bottle and sealed with butyl rubber stopper. A nitrogen headspace was placed on top of the media and the bottles were sterilized by steam. When inoculated from an actively growing culture in a 2 L chemostat, synthesis gas was bubbled through the culture. The headspace was monitored for synthesis gas components and hydrogen sulfide and was replenished with fresh synthesis gas when needed. The bottles were usually shaken at 100 rpm at 30°C.

Syn-Gas Utilization by Mixed SRB

Utilization of syn-gas by mixed SRB culture developed from municipal sewage was investigated in a serum bottle containing minimal salt medium and SO_2 as terminal electron acceptor. The head space of the bottle was then filled with synthesis gas mixture containing 36% H_2 , 47% CO, 10% CO_2 , 5% CH_4 , and balance N_2 . The bottle was inoculated with mixed SRB culture and incubated at 30°C with shaking at 200 rpm. The syn-gas concentration was then regularly monitored using a Gas Chromatograph as described below.

Microbubble Generation and Characterization

Microbubbles are small, surfactant coated bubbles of gas that are generated by creating a gas-liquid interface in a high-shear zone. The bubbles are between 50 μm and 100 μm in diameter and the surfactant coating helps to prevent coalescence by electrostatic repulsion from the diffuse electric double layer around the bubble. In our work, the microbubble dispersions were generated using a spinning disk apparatus first described by Sebba [12]. This microbubble generator (MBG) uses a high speed motor (Talboys #37830, Cole Parmer, Chicago, IL) that spins a 4 cm disk as speeds above 4000 RPM in close proximity to baffles (within 3 mm) to generate a localized high-shear zone. The stainless steel disk and baffles are mounted in 4 L glass vessel with a ground glass lip to fit the headplate. A second headplate mounted above the first supports the motor and allows easy alignment. Stainless steel sealed bearings insure minimal wobble.

The bubble size measurements were performed on a Coulter LS 130 particle size analyzer (Coulter) using laser diffraction. The microbubble foam sample was loaded into both the constant volume module and hazardous fluids module for the instrument. The constant volume module could contain 15 mL of sample and had a magnetic stirrer in the bottom of the cell to maintain a well-mixed system. The hazardous fluids module used a recirculating pump. Dispersion was added to water in each module until 8% to 12% obscuration was obtained. Data was collected for ninety seconds in each case. Between runs the constant volume module was rinsed with double distilled water and the hazardous fluids modules had the recirculating liquid drained, refilled, and filtered.

CSTR and Trickle Bed Reactors

A 2 L Virtis Omni-culture chemostat (Virtis Co., Gardiner, NY) with temperature and agitation control was used as the primary reactor vessel. The vessel headplate was modified for acid/base additions and gas and liquid inlets and outlets. The pH was controlled at 6.8 with a Chemcadet controller with 6 N NaOH and 6 N H_3PO_4 . The reactor was maintained at a temperature of 30°C and agitated at 250 rpm for all experimental runs. The reactor was operated in a continuous mode with a feed rate of fresh MS medium at 0.2 mL/min. To retain biomass in the reactor, a filtration system consisted of two Amicon Diaflo hollow fiber cartridges was attached to the reactor. All pumps used were Masterflex peristaltic. A sparge of 50 mL/min of nitrogen was added to the reactor vessel to strip off the produced H_2S from the reactor. The synthesis gas was fed directly at a rate

of 10 mL/min to the reactor during the control runs through a stainless steel sparger. The flow rate of SO₂ gas fed separately into the reactor was monitored using gas flow meter. In the microbubble-fed system, the permeate from the filters was returned to the MBG, the syn-gas microbubbles were generated by bubbling syn-gas into minimal salt medium containing Tween-20 (240 mg/L) as surfactant. The microbubbles were then fed to the CSTR at a rate of 15 mL/min, which was equivalent to 10 mL/min of synthesis gas as fed during the control run.

The trickle bed reactor consisted of fully jacketed glass column of internal dimensions 2.5 x 30 cm with a total volume of 180 mL and a working volume of 81 mL with BIO-SEP™ beads. BIO-SEP™ beads, encapsulated activated carbon (50-80%) in aromatic polyamide (Aramid) (20-50%) were obtained as the kind gift of Dr. Carl Camp from the DuPont Chemical Co. (Glasgow, DE). The reactor was operated at a temperature of 30°C. A 500 mL bottle with a specially made headplate was used for pH control, H₂S stripping by nitrogen, gas outlet, and ports for continuous operation. The reactor had biomass loaded on to the BIO-SEP beads by operation in a packed bed mode on lactate media. The liquid inside of the reactor was completely recycled. When switched to a synthesis gas feed, the reactor was operated in a trickle bed mode with the liquid and both gas feeds entering at the top of the reactor. Gas samples were taken from a gas disengagement bottle. The reactor was operated in a continuous mode with a fresh minimal salt medium at a feed rate of 12 mL/h. In trickle bed mode, the liquid flow rate across the bed was 600 mL/h.

In all runs the reactor was monitored for sulfite. The off-gas from the reactor was also monitored for H₂S and synthesis gas components. The off-gas flow rates were monitored with a wet test meter for two hour periods.

Analytical

The sulfite in the reactor was analyzed spectrophotometrically by the reaction of fuchsin and formaldehyde in sulfuric acid [13]. The sulfide in the reactor was precipitated using zinc acetate in a basic solution followed by resuspension and measurement using the formation of methylene blue [14].

Hydrogen sulfide in the off gas was analyzed using a gas chromatograph (Hewlett Packard HP 5890 Series II) equipped with a teflon column (30 in x 1/8 in) packed with Super Q (80/100 mesh) (Alltech, Waukegan, WI). Temperatures of the column, injection port, and thermal conductivity detector were 70°C, 125°C, and 125°C respectively. The carrier gas was helium at 25 mL/min. The calibration was based on 1%, 5%, and 10% H₂S in nitrogen standards. Synthesis gas components were measured using a gas chromatograph (Hewlett Packard HP 5890 Series II) equipped with a HP PLOT molecular sieve 5 Å capillary column (30 m x 0.32 mm) with a 12 µm film thickness. Temperatures on the column, injection port, and thermal conductivity detector were 55°C, 100°C, and 240°C respectively. Liquid samples were filtered through a 0.22 µm syringe filter and analyzed by gas chromatography using a HP 5890 Series II with a HP WAT (crosslinked PEG) capillary column (30 m x 0.53 mm) with a 1.0 µm film thickness. The column temperature program was initially 70°C followed by ramping to 200°C at 25°C/min with a 1.2 min hold then followed by ramping to 225°C at 25°C/min with a 3.0 min hold. The injection port temperature was 245°C while the flame ionization detector was 265°C.

Results and Discussion

Syn-Gas Utilization by Mixed SRB

Initially, a decrease in CO concentration was observed with no change in H₂ concentration. However, hydrogen sulfide was detected during this time in the head space of the serum bottle. This indicates that the CO was utilized by certain type of bacteria and produced H₂ as shown in the equation below:



With limited SO₂ reduction due to a possible CO inhibition at higher concentration, the H₂ concentration declined only after the CO concentration was less than about 5% in the mixture. This suggests that the mixed culture developed from sewage solids would be

able to use CO as sole carbon and energy source and produce H₂. Kinetically, the CO utilization was much faster than H₂ utilization by SRB cultures.

Serum bottle experiments with mixed SRB showed that we could switch between lactate and syn-gas for carbon and energy source that would help us to start the reactor operation more quickly.

CSTR with syn-gas feed

The CSTR in the control mode in which the syn-gas was fed directly into the reactor was able to convert 1.2 mmol SO₂/h•L with no sulfite detected in the effluent (Fig. 1). The off-gas analysis through GC showed 100% conversion of SO₂ into H₂S. With continuous N₂ purging in the liquid medium, the sulfide concentration in the aqueous phase was measured to be less than 5 mg/L. When the SO₂ feed was increased above 1.2 mmol/h•L, sulfite accumulation of greater than 25 mg/L was observed in the reactor medium. This indicated that the reactor reached the maximum productivity of 1.2 mmol SO₂/h•L under the operating conditions. The synthesis gas content in the feed and the off-gas showed the stoichiometric conversion of 1.8 mol H₂ and 2.3 mol CO per mol of SO₂. The reactor was then operated at 1.2 mmol/h•L, for 3 d and switched over to microbubble-fed system. With syn-gas fed as microbubbles, the SO₂ feed rate was increased incrementally and the maximum productivity of 2.1 mmol/h•L was obtained with 100% conversion to H₂S in 33 h. The biomass concentration in the reactor prior to the microbubble operation was 5 g/L. The increase of productivity from 1.2 to 2.1 mmol/h•L within the span of 33 h at the same biomass concentration of 5 g/L indicated that the mass transport of syn-gas was the limiting parameter in the above process.

Trickle-bed reactor with syn-gas feed

Initially, the immobilization of mixed SRB cells in BIO-SEP beads in a trickle-bed reactor was started-up with lactate medium as described earlier. This was achieved in 14 d. Following the immobilization, the reactor was fed with syn-gas at a rate of 10 mL/min as a sole carbon and energy source and 5% SO₂ at rate of 4 mL/min (2.7 mmol/h•L). The immobilized SRB cells grown on lactate medium were able to switch to syn-gas at once. The SO₂ feed rate was then increased incrementally with no sulfite detected in the effluent. As shown in Fig. 2, complete conversion of SO₂ into H₂S was achieved at a maximum SO₂ feed of 8.8 mmol/h•L with syn-gas utilization of 1.0 mol H₂ and 1.2 mol CO per mol of SO₂. This compares to previous studies which achieved 4.3 mmol SO₄²⁻/h•L [9] and 0.5 mmol/h•L [10] with synthesis gas as feedstock.

Conclusion

The model coal synthesis gas containing 36% H₂, 47% CO, 10% CO₂, 5% CH₄, and balance N₂ has been found as a low-cost feedstock for mixed SRB in the desulfurization processes. With syn-gas fed as microbubbles, productivity in the CSTR increased from 1.2 to 2.1 mmol/h•L in 33 h. This has been observed at the same biomass concentration of 5 g/L. This shows the mass transport limitation in the above process. In the trickle bed reactor, maximum productivity of 8.8 mmol/h•L was achieved with less carbon and energy requirement (1 mol H₂ and 1.2 mol CO per mol of SO₂) indicating better surface to volume ratio with cells immobilized in the pores of polymeric beads. The mass transfer coefficients in these systems will be determined in future studies to develop better reactor configuration for biodesulfurization of flue gases and other sulfur wastes.

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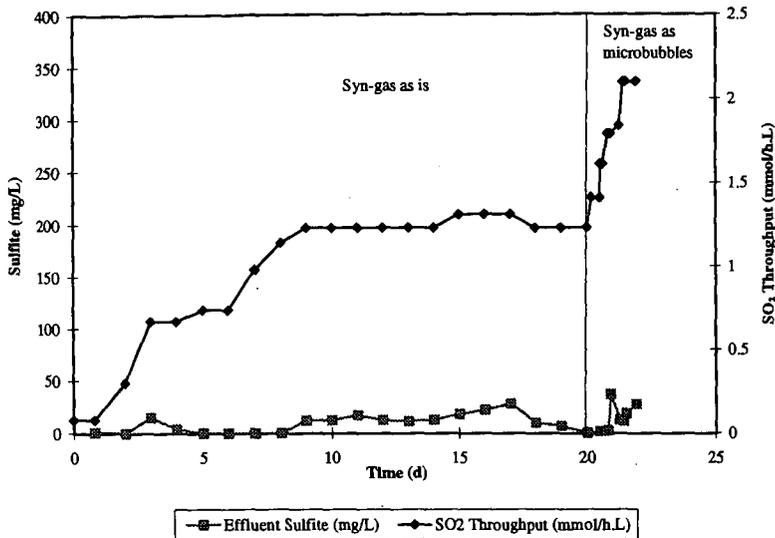


Figure 1. Sulfite conversion in a CSTR with syn-gas as feedstock. With syn-gas fed as microbubbles, the reactor productivity was increased from 1.2 to 2.1 mmol/h.L in 33 h.

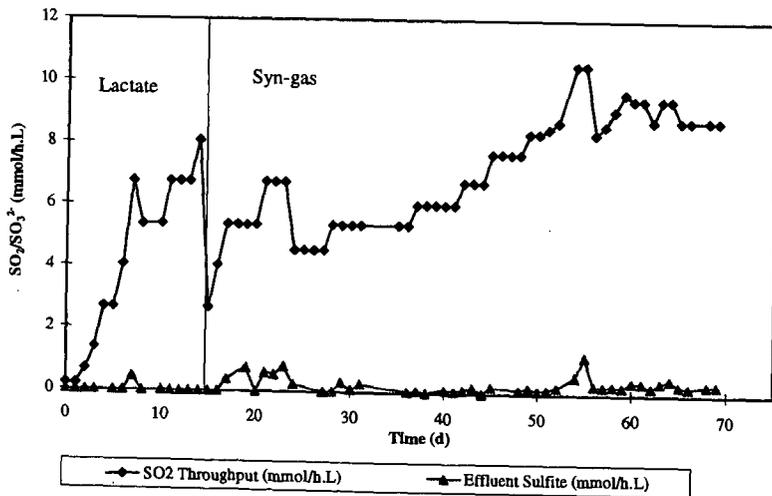


Figure 2. Sulfite conversion in a trickle-bed reactor with mixed SRB immobilized in BIO-SEP™ beads. The liquid medium and gas mixture (syn-gas and SO₂) were fed co-currently at the top of the reactor.