



Biological oxidation of hydrogen sulfide in mineral media using a biofilm airlift suspension reactor

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ABSTRACT

Hydrogen sulfide (H₂S) removal in mineral media using *Thiobacillus thio-parus* TK-1 in a biofilm airlift suspension reactor (BAS) was investigated to evaluate the relationship between biofilm formation and changes in inlet loading rates. Aqueous sodium sulfide was fed as the substrate into the continuous BAS-reactor. The reactor was operated at a constant temperature of 30 °C and a pH of 7, the optimal temperature and pH for biomass growth. The startup of the reactor was performed with basalt carrier material. Optimal treatment performance was obtained at a loading rate of 4.8 mol S²⁻ m⁻³ h⁻¹ at a conversion efficiency as high as 100%. The main product of H₂S oxidation in the BAS-reactor was sulfate because of high oxygen concentrations in the airlift reactor. The maximum sulfide oxidation rate was 6.7 mol S²⁻ m⁻³ h⁻¹ at a hydraulic residence time of 3.3 h in the mineral medium. The data showed that the BAS-reactor with this microorganism can be used for sulfide removal from industrial effluent.

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1. Introduction

Hydrogen sulfide (H₂S) is a major environmental contaminant from many industrial effluents such as petroleum refining (Henshaw, 1990), pulp and paper manufacturing (Wani et al., 1999) and food processing (Chung et al., 2001). Anaerobic conversion of sulfate and sulfite compounds to hydrogen sulfide occurs frequently in wastewater treatment plants, causing problems of corrosion and strong unpleasant smells (Cheerawit et al., 2009). Because of these problems, there are strict regulations to control and eliminate the emission of this toxic compound from wastewater treatment plants and other emission sources.

The conventional methods to remove hydrogen sulfide are physico-chemical processes based on steam/air stripping followed by chemical oxidation and precipitation stages. These systems are expensive due to their high energy demand and operating costs (Chung et al., 2006). Biological treatment processes are often used to overcome these difficulties (Oyarzun et al., 2003). Many microorganisms can grow chemolithotrophically on sulfide compounds, including hydrogen sulfide. They obtain energy for growth by oxidizing sulfide components. Several bacterial species have been evaluated for their sulfide oxidation properties (Syed et al., 2006). *Thiobacillus thio-parus* was used for hydrogen sulfide treatment of industrial wastewater (Kanagawa and Mikami, 1989; Chung et al., 1996; Chung et al., 1997; Qiu et al., 2006; Cho et al., 1991; Vlasceanu

et al., 1997). This method is reported to be inexpensive and it does not produce additional pollution. *T. thio-parus* can oxidize sulfide into elementary sulfur under suitable physical, chemical and operational conditions (Qiu et al., 2006). This kind of bacterium is also capable of degrading other sulfur containing compounds such as methanethiol, dimethylsulfide, and dimethyldisulfide. Some other species evaluated for sulfur reduced compounds removal are *T. denitrificans*, *T. ferrooxidans*, and *T. novellas* (Ma et al., 2006; Pagella and De Faveri, 2000; Cha et al., 1999).

Different types of bioreactors have been used for H₂S removal by chemotrophic bacteria. These include gas-fed batch reactors (Janssen et al., 1995), fixed-film upflow reactor, biorotor, continuous-flow reactors (Buisman et al., 1990), bioscrubbers (Nishimura and Yoda, 1997; Mesa et al., 2002), biofilter (Malhautier et al., 2003; Schieder et al., 2003; Jung et al., 2008; Cheerawit et al., 2009), and biotrickling filter (Cox and Deshusses, 2002; Sercur et al., 2005; Juan and Rakesh, 2008).

Although, well-developed biological domestic wastewater treatment processes have a great treatment capacity and produce a high effluent quality, these kinds of suspended growth system have some inherent drawbacks, such as high energy consumption, large reactor volume and the potential for sludge bulking. New biological wastewater treatment processes with high treatment efficiency, low energy consumption and stable operation have been proposed to overcome the limitations of the conventional systems. Biofilm Airlift Suspension (BAS) reactor is a novel biological wastewater treatment process that has been evaluated extensively (Heijnen and Van Loosdrecht 1991, 1993; Nicoletta et al., 2000). It

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has been proven that this type of reactor offers advantages (such as high hydraulic loading rate, high biomass concentration, ideally mixed, high biofilm surface area, and high conversion capacity) over the activated sludge process and other biofilm reactors while maintaining their common merits. Inert particulates, such as sand, activated carbon, or ceramic materials, may be used as carriers in the reactor to support the growth of microorganisms.

The objective of this work is to develop a biofilm airlift suspended reactor using basalt as solid support for *T. thioparus* (PTCC 1668) for the first time to directly treat liquid solutions containing high concentrations of H_2S in mineral media.

2. Methods

2.1. Reactor and operating conditions

A laboratory scale airlift reactor with a volume of 4.2 l made of Shott glass was used in this study. Fig. 1 shows a schematic representation of the experimental setup.

Before startup, the reactor was filled with the media (with a sulfide concentration of $2 \text{ mmol S}^{2-}/\text{l}$) and 65 g/l basalt as carrier particles. The reactor was inoculated with a culture of *T. thioparus* TK-1, at an initial total concentration of 10 mg DW/l , and operated batch wise. Continuous feeding was initiated after 24 h at a residence time of 24 h, the aeration rate in this period was 1.7 l min^{-1} and the sulfide concentration in the feed solution was constant at $2 \text{ mmol S}^{2-} \text{ l}^{-1}$ (corresponding to the loading rate of $0.083 \text{ mol S}^{2-} \text{ m}^{-3} \text{ h}^{-1}$).

The temperature was maintained at $30 \pm 1^\circ\text{C}$ using a thermostated water jacket. The pH of the influent was 7. Initially, the air was charged into the reactor by global air stone. Small basalt particles with a mean particle diameter of 0.3 mm , density of 3 kg l^{-1} and a settling velocity of 50 m h^{-1} were used. Sulfide was always added to media as a solution of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and was present as HS^- and H_2S . When air is sparged into the riser of the reactor from the bottom, a pressure difference is formed between the riser and the downcomer, leading to an internal circulation of media, carriers and bubbles, upflow in the riser where the pressure is lower and down flow in the downcomer where the pressure is higher. Under

these conditions, the basalt was suspended homogeneously in the airlift. A three-phase separator is located on the top of the reactor and the mixture of air, water, and carriers are separated within the separator. Before their use, the basalt particles were treated with $1 \text{ M H}_2\text{SO}_4$ solution for 24 h and washed continuously in order to remove acid soluble salts till the solution becomes neutral.

The effect of temperature on H_2S removal efficiency was conducted in a range from 25 to 45°C . During the experiment, the sulfide loading rate and the hydraulic retention time were $4.8 \text{ mol S}^{2-} \text{ m}^{-3} \text{ h}^{-1}$ and 3.3 h , respectively.

2.2. Microorganism and media

T. thioparus TK-1 was obtained from a Persian type culture collection (PTCC, 1668). The optimal pH for bacterial growth was reported to be in the range of 5 until 9 and the optimum temperature was 30°C (PTCC, 2008). The liquid medium used was a modification of the thiosulfate medium (PTCC 1668) recommended for increasing biomass, composing of (in g l^{-1}): K_2HPO_4 2.0, KH_2PO_4 2.0, and NH_4Cl 0.4, Na_2CO_3 0.4, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 0.2, and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ 5.0 and tap water 1000.0.

2.3. Analytical procedures

Hydrogen sulfide was analyzed using silver/sulfide ion electrodes (Cole Parmer, Cat. No. 27502–41), and sulfate by a turbidimetric method ($4500\text{-SO}_4^{2-} \text{ E}$) with a spectrophotometer (Spectronic 401, Milton Roy). Mixed liquor volatile suspended solids (MLVSS) was determined according to the Standard Method 2540E (Clesceri et al., 1998). Biofilm development was determined by removing a sample from the reactor. The mean biofilm diameter and standard deviation were calculated from about 50 randomly selected particles observed with an Olympus PMG 3-AN microscope (Lee et al., 2004). Biomass concentration on the carrier was determined by MLVSS analyses. To measure biomass content of the biofilm, the sample was placed on fiber glass paper and dry weight was determined after drying for at least 24 h at 103°C . The carrier content was measured by burning off the biomass in a furnace for 1 h at 550°C . The measurements were corrected for

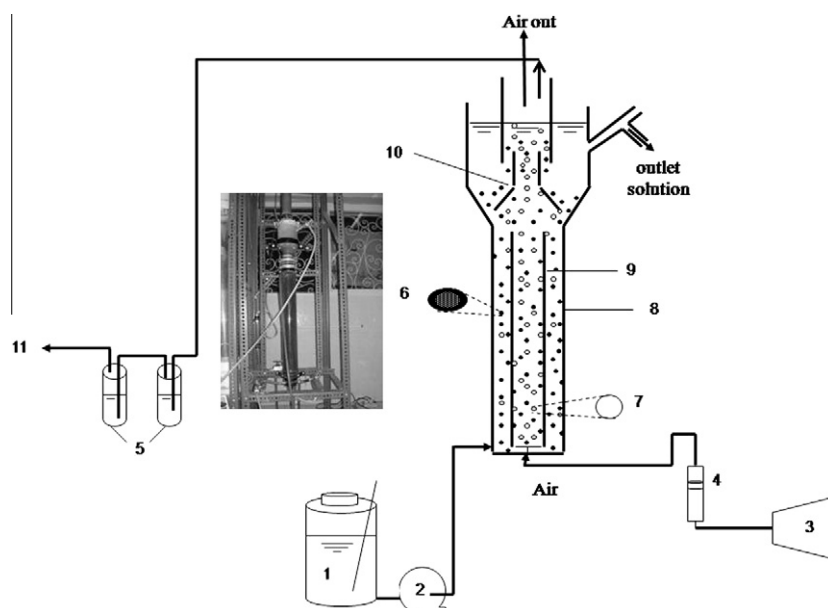


Fig. 1. Schematic diagram of the experimental setup. (1) Sulfide stock tank; (2) peristaltic pump; (3) air compressor; (4) air flow meter; (5) zinc acetate solution; (6) biofilm on carrier; (7) air bubbles; (8) downcomer; (9) riser; (10) three-phase separator and (11) to vacuum pump.

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