



H₂S Removal from Sour Water in a Trickle Biofilter

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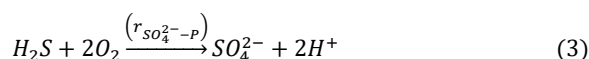
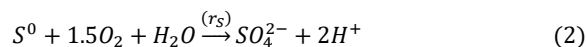
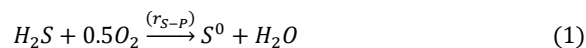
Abstract

Long term desulfurization of sour water was studied in a co-current trickling biofilter (BTF) to find out an alternative to the traditional methods (stripping in a packed or tray columns) being used in the gas and oil refineries. Microorganisms from an operating trickling biofilter, treating low levels of H₂S (up to 5 g S-H₂S m⁻³) and organic pollutants, were taken, enriched immobilized on the packing materials. A critical elimination capacity (EC) of 151g S-H₂S m⁻³h⁻¹ was achieved during stepwise increase of sulfide concentration from 10 to 50 g S-H₂S m⁻³. H₂S measurement along the bed showed that the most significant sulfide removal occurred at the top section of the BTF. Besides the H₂S concentration, the effect of liquid velocity and aeration rate was investigated during two independent experiment. Results showed that aeration rate did not increase sulfate production and sulfate selectivity should be improved by regulating of the liquid velocity. It was concluded that biological treatment can be used as a viable alternative to traditional methods for H₂S removal from sour water.

Keywords: Sour water, Hydrogen sulfide, Biological removal, Trickle biofilter

1 Introduction

Sour water is defined as any wastewater that contains malodorous materials, usually sulfur compounds such as H₂S, dimethyl sulfide, dimethyl disulfide, and methanethiol, etc. Sour gas processing, oil refining, Claus tail gas units, gasification and other thermal processes are some major sources of sour water. H₂S constitutes the main pollutant in sour water and needs to be controlled for its adverse health and environmental effects. It is a colorless, flammable, and corrosive gas, being extremely toxic to living organisms. In petroleum and gas refineries, H₂S is typically removed from sour water by steam stripping in packed or tray columns. These systems are expensive due to their high energy demand, and operating costs. Biooxidation of H₂S can be used to overcome the difficulties related to conventional methods of H₂S removal. In aerobic biooxidation, dissolved H₂S is oxidized to elemental sulfur as an intermediate product and/or sulfate as a final product depending on the availability of dissolved oxygen (DO) and substrate [1] (equations 1-3).



The bacteria of sulfur cycle and their applications were discussed by Tang et al. [2] in a review paper. A wide variety of sulfur oxidizing bacteria (SOB) have been frequently assessed based on their growth conditions, carbon and electron sources, the sulfide-oxidizing pathway, and the location of bio-sulfur storage. Most studies, however, have been focused on biogas streams [3-5], and polluted air [6-8]. Chemotrophic biooxidation of H₂S from sour water in a trickling biofilter (BTF) is still lacking in literature. The removal efficiency (RE) of a BTF is influenced by various parameters such as packing materials, gas contact time, pH, gas-liquid flow pattern, nutrient availability, and substrate inhibition. Besides the elimination capacity (EC), the sulfate selectivity (produced sulfate/degraded sulfide) is also important in BTFs design. Sulfur accumulation inside the biofilm due to the partial oxidation can clog the bed and significantly reduce the RE of the BTFs. Therefore, a well-designed BTF should have a high EC as well as high sulfate selectivity for a long term operation. The aim of this work was to investigate the H₂S removal from sour water in an aerobic BTF and to assess the influence of the operating

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parameters such as sulfide loading rate (LR) and empty bed residence time (EBRT) on the BTF performance.

2 Materials and Methods

2.1 Experimental set-up

The laboratory scale system for sour water treatment is shown in Figure 1. The BTF (1) is a Plexiglas column of 90 mm diameter and 600 mm height. It consists of 3 sampling ports (2) to measure H_2S concentration and sample microorganisms. Sour water (3) and stripped sour water (4) from a gas plant were mixed to provide sour water with desired concentrations (5). An air blower (6) was used to supply air and a diaphragm pump (7) trickled the sour water over the BTF. Two rotameters were used to measure the flow rates of liquid (8) and gas phases (9). Air flow was firstly passed through a stripped sour water container to increase the DO concentration in the liquid phase. The outlet air from the stripped sour water container was passed through the BTF under a co-current flow pattern. After passing through the BTF, the treated sour water was collected in a separate container (10) and exhaust air was sent to a caustic column (11) to ensure that H_2S was not released to the environment.

2.2 Materials

Microorganisms from an operating trickling biofilter, treating low levels of H_2S (up to $5 \text{ g S-H}_2\text{S m}^{-3}$) and organic

pollutants, were taken and enriched by transferring to the *Thiobacillus* medium which contained 2.0g KNO_3 , 1.0g NH_4Cl , 2.0g KH_2PO_4 , 2.0g NaHCO_3 , 0.8 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 5.0 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and 1.0 mL trace element in 1000 mL distilled water and the pH was adjusted to 6.5 with 4MNaOH. The trace element solution contained 50g $\text{Na}_2\text{-EDTA}$, 7.34g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 5.0g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 2.5g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 2.2g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 0.5g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, 0.2g $\text{CaSO}_4 \cdot 5\text{H}_2\text{O}$ and 11.0g NaOH in 1000 mL of distilled water. To enrich the culture, 5 mL of the mixed culture sample was inoculated into 100mL of the *Thiobacillus* medium and incubated at 35°C for 14 days. The increase in turbidity of the medium was interpreted as microbial growth. After then 10 mL of the medium was inoculated into 100 mL of fresh medium and incubated for 14 days once again. Samples were streaked on solid medium, incubated at 35°C , and single colonies of the dominant species were assessed for morphological and physiological properties as details in Table 1.

The immobilization process of bacterial cells was initiated by transferring the packing materials into *Thiobacillus* mineral salts medium (MSM) containing the microorganisms, and then the column were packed with cell laden packing materials. For one week, the BTF was fed with thiosulfate and thereafter sour water was sent to the filter. To avoid cells washout from the bed, the liquid flow was fully recycled to the BTF during two weeks.

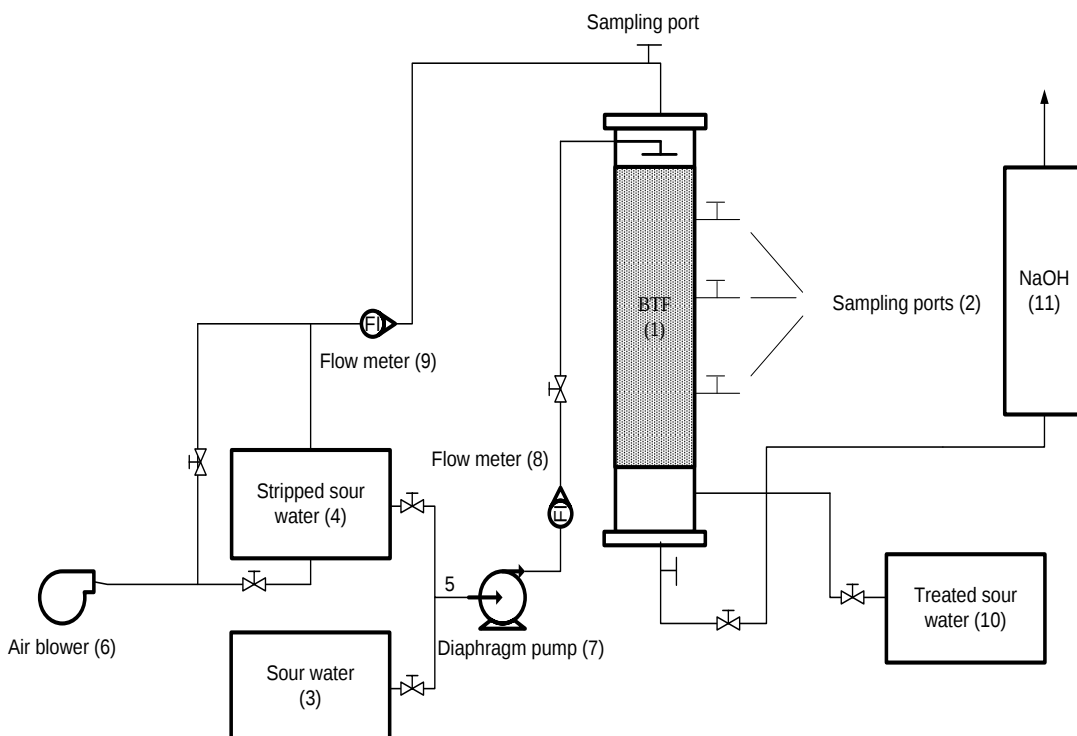


Fig. 1: Schematic of the experimental setup: 1. The BTF; 2. Sampling ports; 3. Sour water container; 4. Stripped sour water container; 5. Mixed sour water; 6. Air blower; 7. Diaphragm pump; 8. Liquid flow meter; 9. Gas flow meter; 10. Treated sour water container; 11. Caustic column.

Table 1: Properties of *Thiobacillus* sp. enriched from operating BTF

Colony Morphology	Irregular, grey
Size (μm)	Short rod
Gram-staining	0.5×1.5-2
	Negative

2.3 Methods

H₂S concentration in the gas phase was determined using gas tube sensors (Gastec Co.). Total dissolved sulfide (TDS) was analyzed using silver/sulfide ion electrodes (Metler, Cat. No. SC-DMI141). Sulfate concentration was measured by a turbidimetric method.

2.4 Experimental conditions

Reference operation conditions was defined as the treatment of real sour water containing 20g S-H₂S m⁻³ of H₂S at a TLV of 4.72 m h⁻¹ (LR=157 g S-H₂S m⁻³ h⁻¹) and an EBRT of 457 s. Experimental conditions for co-current systems are summarized in Table 2. After 20 days of steady operation at reference conditions, 3 experiments were carried out and the effects of H₂S inlet concentration, gas and liquid flow rates were studied. During experiment E1, H₂S inlet concentration was progressively increased from 10 to 50 g S-H₂S m⁻³ at constant liquid and gas flow rates (sulfide LR from 78 to 393 g S-H₂S m⁻³ h⁻¹) for period of 5 days. During experiment E2, at constant H₂S inlet concentration of 20 g S-H₂S m⁻³, the liquid flow rate was increased stepwise from 0.015 to 0.075 m⁻³ h⁻¹ (sulfide LR from 78 to 393 g S-H₂S m⁻³ h⁻¹). During experiment E3, at constant H₂S inlet concentration and liquid flow rate (constant LR), the air flow rate was increased stepwise from 0.01 to 0.04 m⁻³ h⁻¹ to evaluate the effect of the gas contact time on elimination capacity of the BTF. Steady state conditions in the BTF was ensured at the end of each step by measuring a constant EC at the end of each experiment.

3 Results and discussion

3.1 Effect of the inlet concentration

The RE during experiment E1 decreased from 96-99% at the lowest LR (78 g S-H₂S m⁻³ h⁻¹) to 79-82% at the highest LR tested (393g S-H₂S m⁻³ h⁻¹). During this test, the critical and maximum ECs were 151 and 321 g S-H₂S m⁻³ h⁻¹, respectively as depicted in Fig.2. The critical EC is comparable to the values reported by Montebello et al. [9] (160 g S-H₂S m⁻³ h⁻¹) for biogas treatment of 2000 to 10000 ppm_v of H₂S in a randomly packed BTF and Lee et al. [10] (160 g S-H₂S m⁻³ h⁻¹) for removal of 200 to 2200 ppm_v of H₂S in a BTF packed with porous ceramic materials. However, the maximum EC of the BTF is considerably higher than the value obtained by Montebello et al. [9] (223 g S-H₂S m⁻³ h⁻¹) (223 g S-H₂S m⁻³ h⁻¹) since the EBRT in their study (120 s) is significantly lower than the value of the present work at the reference conditions (458 s). Besides the elimination capacity, the sulfate selectivity also is a determinative parameter affecting the BTFs performance treating sulfides. Sulfur accumulation inside the biofilm due to the partial oxidation of sulfides can clog the bed and significantly reduce the EC of the biofilters. Sulfate selectivity for a specific microorganism mainly depends on substrate and oxygen availability (ratio DO/S²⁻). Theoretically, higher DO/S²⁻ is more desirable for sulfate production because formation of one mole sulfate needs two moles oxygen, while one mole sulfur only needs half mole oxygen.

Table 2: Experimental conditions

Experiment	C_{L,H_2S} (g S-H ₂ S m ⁻³)	Q_L (m ³ h ⁻¹)	LR (g S-H ₂ S m ⁻³ h ⁻¹)	Q_G (m ³ h ⁻¹)	Duration (days)
E1	10	0.03	78	0.03	5
	20		157		
	30		235		
	40		314		
	50		393		
E2	20	0.015	78	0.03	5
		0.030	157		
		0.045	235		
		0.060	314		
		0.075	393		
E3	20	0.02	157	0.03	4
				0.04	
				0.05	
				0.06	

The ratio DO/S^{2-} depends on sulfide and oxygen solubility in the liquid phase, and external mass transfer coefficients. Solubility is directly linked to Henry's law constants which depends on pressure and temperature. External mass transfer coefficients are influenced by the fluid flow characteristics in both gas and liquid phases and are therefore related to Reynolds number. For a specific system with constant operating conditions (pressure and temperature), the ratio DO/S^{2-} becomes only mass transfer depended. At the operating conditions usually occurred in the BTFs, the liquid-gas mass transfer for both O_2 and H_2S is controlled by the liquid phase which depends on liquid velocity. Therefore, the main parameter affect the ratio DO/S^{2-} in the BTFs is the trickling liquid velocity (TLV). During experiment E1, sulfate selectivity of the BTF decreased from 99% at the beginning of the E1 to 65% at the end of the test. Such sulfate selectivity is higher than the values reported by Montebello et al. [9, 11] despite the higher TLV used in their study. This can be due to various biomass with different sulfur production ability. In fact, bacteria can obtain their energy and electron from different oxidation pathways (Eqs 1-3). Besides the ratio DO/S^{2-} , the selection of each path is depended on type of microorganism. Some bacteria such as *Thiothrix* sp. oxidizes sulfide to sulfur regardless of the ratio DO/S^{2-} [12] while a mixed culture dominated by *Thiobacillus* sp. oxidizes a part of sulfide to sulfate even at low sulfide concentrations [13].

3.2 H_2S removal along the bed

H_2S removal efficiency throughout the BTF bed height during E1 is depicted in Fig. 3a. The RE was calculated at the three sections (1/3, 2/3, 3/3 of the BTF), corresponding to the top, middle and bottom sections of the filter. Results showed that the most significant H_2S removal occurred at the top section of the filter. This was attributed to high oxygen availability at the top section due to the preliminary aeration of sour water. This results also indicated that at the reference conditions, around 71% and only 9% of RE occurred at the top and bottom section, respectively. This means that operating the BTF at reference conditions for a long period can lead to the starvation conditions for biomass and consequently decrease of the microorganisms' colonies in the bottom section of the reactor.

The H_2S concentration of sour water along the bed is shown in Fig. 3b. As abovementioned the most part of H_2S was degraded at the top section of the BTF which caused H_2S concentration dropped significantly in this section. In many industrial cases, it is not required to completely removed H_2S from sour water. For example, desulfurization of sour water in the gas plants usually does not require of complete H_2S removal since biomass of the downstream unit (waste water treatment) can tolerate H_2S up to $5 \text{ g S-H}_2\text{S m}^{-3}$. Therefore, a sour water containing $20 \text{ g S-H}_2\text{S m}^{-3}$ can be treated in a BTF with one third size of the BTF used in this study.

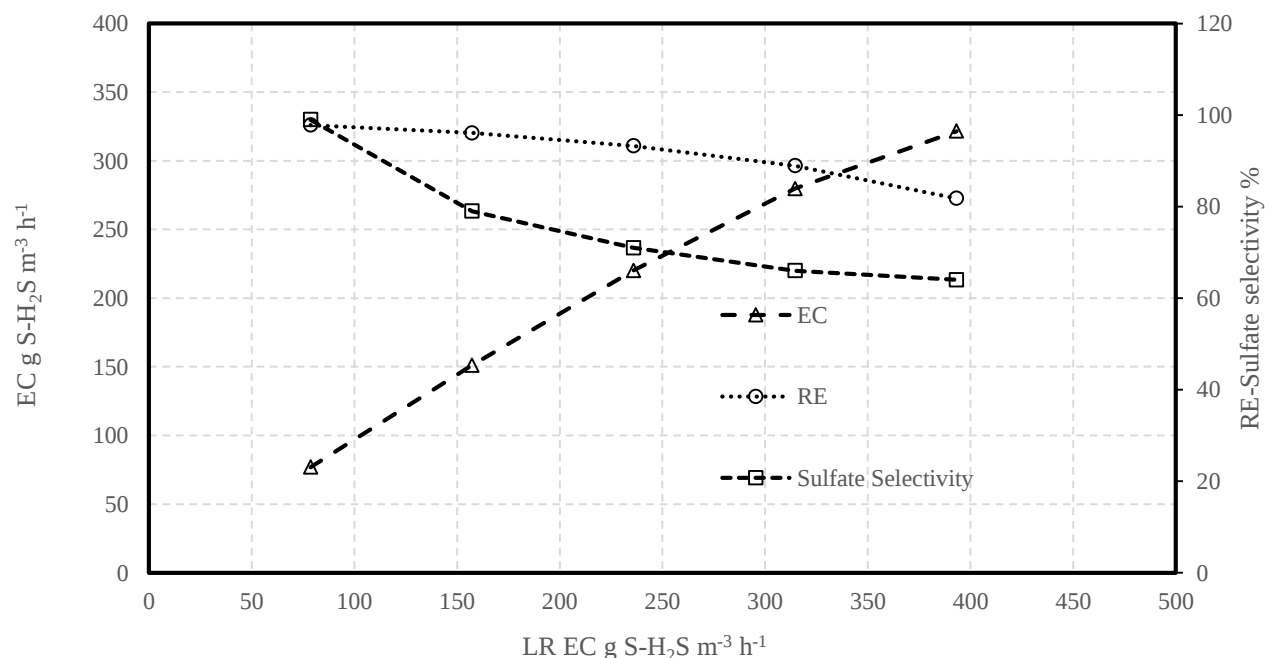


Fig. 2: Elimination capacity and removal efficiency versus H_2S LR during E1

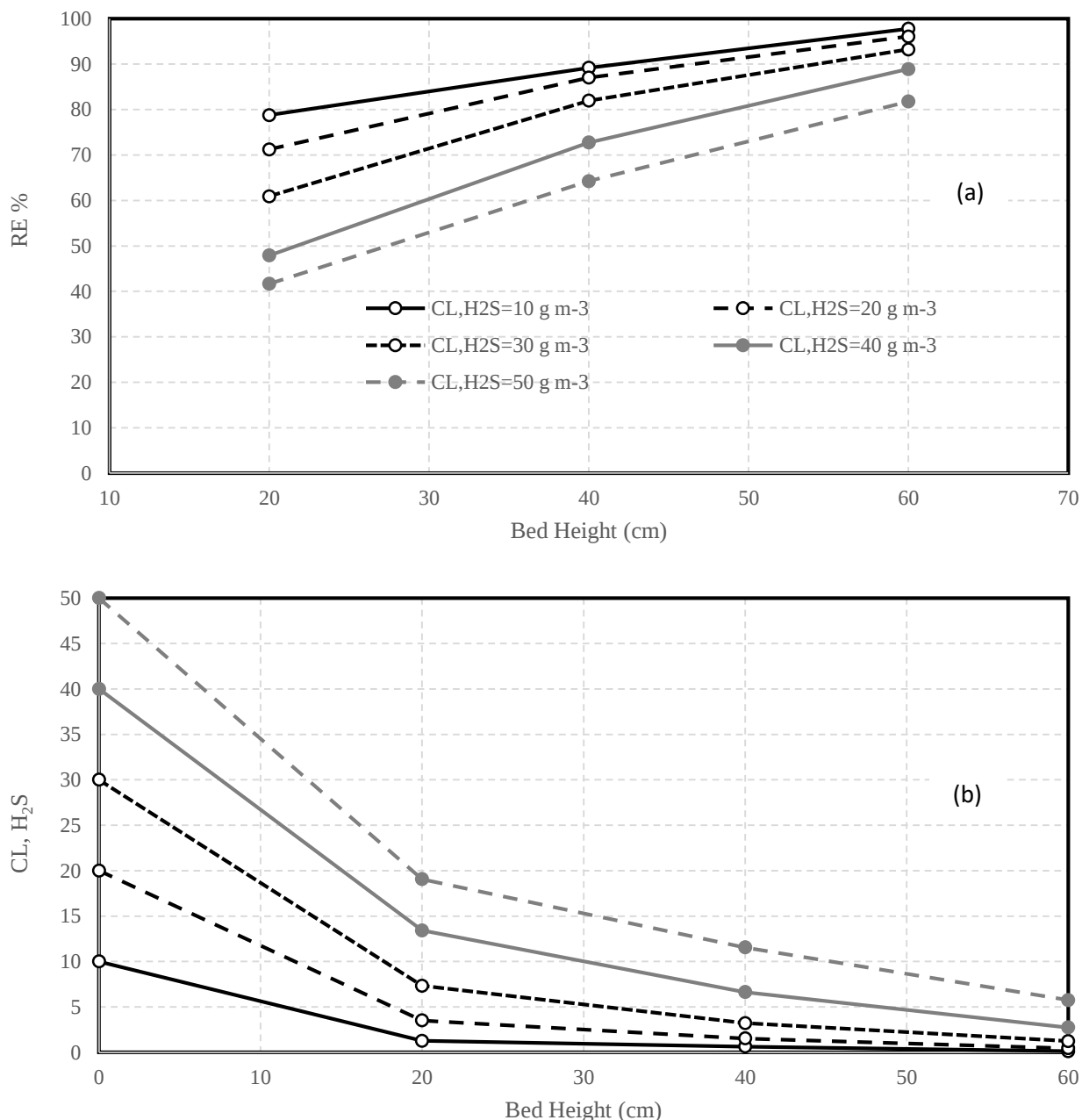


Fig. 3: H_2S removal along the bed height during E1, (a) RE, (b) H_2S concentration in the sour water

3.3 Effect of TLV

The effect of TLV on the reactor performance has been studied in biofilters for H_2S removal from gas streams. In gas streams desulfurization, TLV does not affect the LR and the aim of its regulating is mainly to increase gas-liquid mass transfer coefficient and to avoid sulfur accumulation due to oxygen limitation [13]. In sour water treatment, however the LR is influenced by the liquid velocity as well as inlet concentration. The effect of TLV on the BTF performance in this study was assessed during E2. Like experiment E1, the LR was increased stepwise from 78 to 393 g S- H_2S m⁻³h⁻¹

¹, by increasing the liquid flow rate from 0.015 to 0.075 m³h⁻¹. As depicted in Fig 4, during this experiment, RE decreased from 95-98% at the beginning of the test to 84-87% at the highest LR tested. During this experiment, the critical EC was similar to the obtained during E1, however the maximum EC was improved by 7% (343.87 g S- H_2S m⁻³h⁻¹). The sulfate selectivity during E2, decreased from 91% to 73%. The sulfate selectivity at the highest loading rate tested during E2 is 9% higher than the value obtained at the same loading rate during E1. This result showed that at the high sulfide loading rates, where BTFs are usually oxygen mass

transfer limited, decrease of gas-liquid external mass transfer resistance by increase of the TLV can be an effective method to increase both elimination capacity and sulfate selectivity.

3.4 Effect of gas contact time

The effect of EBRT on the biofilter performance has been repeatedly studied for H_2S removal from energy-rich gas streams and various EC and critical EBRT have been reported [9, 14, 15]. In gas streams treatment, reduction of EBRT increases the LR, while in sour water desulfurization,

LR is controlled by liquid stream, and gas phase (aeration) is just used to provide oxygen as an electron acceptor in aerobic systems. The influence of the EBRT on the BTF performance in this study was assessed during E3 in which EBRT decreased from 458 s to 229 s. As depicted in Fig. 5, during this test the BTF removal efficiency was decreased from 95-97% to 88-90%. Similar trend was found by Chaiprapat et al. [15] who reported a decrease of sulfide RE from 80-90% to 30-40% when the EBRT decreased from 313 to 78 s.

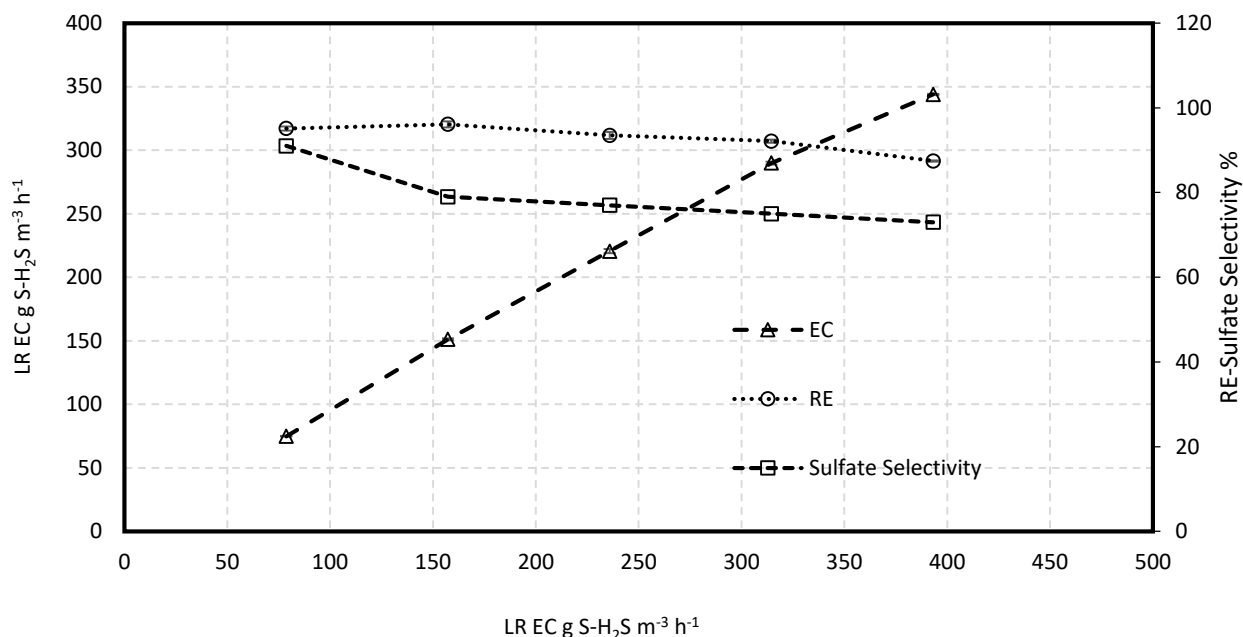


Fig. 4: Elimination capacity and removal efficiency versus H_2S LR during E2

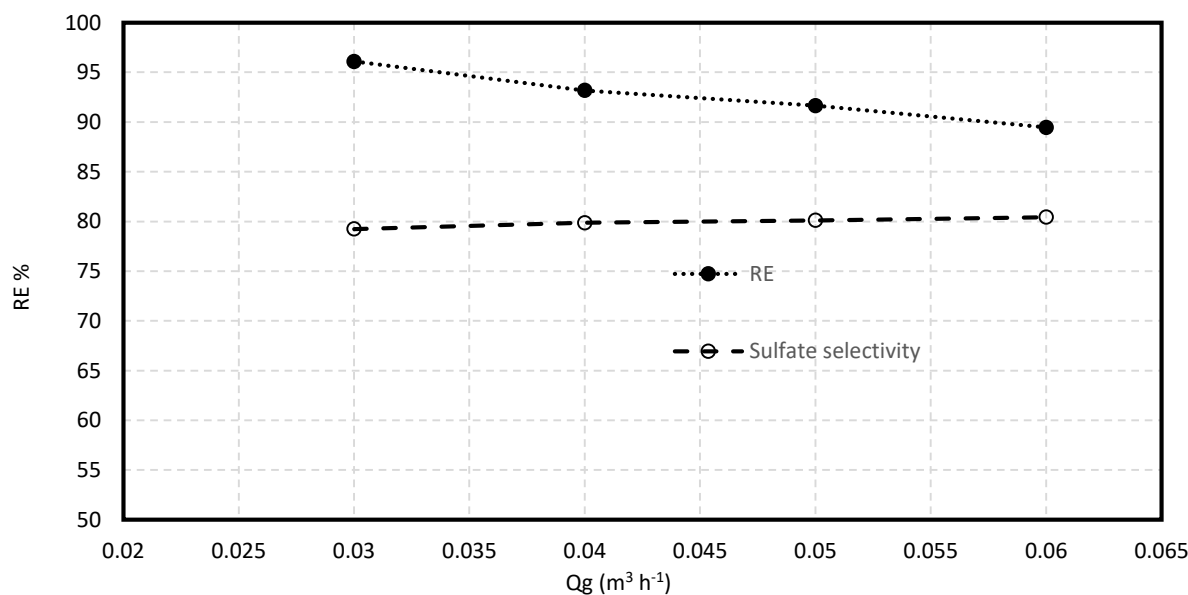


Fig. 5: Removal efficiency and sulfate selectivity versus gas flow rate

Reduction of removal efficiency due to decrease of EBRT was related to mass transfer limitation due to low solubility of both H_2S and O_2 . The sulfate selectivity during E3 was almost constant (79%) reflecting that aeration rate does not affect the sulfate selectivity. This results indicated that in sour water treating, the aeration rate should be kept as low as possible and oxygen mass transfer should be improved by TLV regulating.

2 Conclusion

Biofilters were demonstrated to be an effective alternative to the traditional methods for removing H_2S from energy-rich gas streams and polluted air. In this study, a BTF was used to remove H_2S from sour water and the effects of inlet concentration, TLV and gas contact time on the performance of the BTF were investigated. The sulfate selectivity during all tests was also assessed. Results showed that biological treatment can be used as a viable alternative to traditional methods (stripping in a packed or tray columns) for H_2S removal from sour water. The BTF showed a high sulfate selectivity compared to previous studies which was referred to tendency of microorganism to fully oxidized H_2S to sulfate. Results also indicated that the most significant H_2S removal occurred at the top section of the BTF which was attributed to the high oxygen availability at the top section due to the preliminary aeration of sour water.

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Ethical issue

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

Authors' contribution

All authors of this study have a complete contribution for data collection, data analyses and manuscript writing

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