

Reducing Volatile Organic Compound Emissions Using Biotrickling Filters and Bioscrubber Systems

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ABSTRACT

A comparative study was conducted for differentiating between attached and suspended growth, represented by a lab-scale biotrickling filter and bio-scrubber under anoxic conditions, respectively. However, malodorous ethanethiol gas (ET) that was categorized as one of the volatile organic sulfur compounds (VOSCs) was studied using a variety of settings and parameters. In contrast, NO_3^- can be used as an electron acceptor in the bioconversion of ET gas to elemental sulfur and/or sulfate when no oxygen is available. Empty bed residence times (EBRTs), gas to liquid ratios (G/Ls) (40, 60, 80, 100, 150), and inlet concentrations (150, 300, 800, and 1500 mg/m^3) were all investigated in relation to ET removal efficiency (RE) (30, 60, 90, and 120 s). While the G/L ratio of 80 resulted in efficient ET removal (more than 90.8% for 150 mg/m^3 of inlet concentration), it could only achieve the extraction of 80.6% for 1500 mg/m^3 of inlet concentration at a fixed EBRT of 60 s. These results were based on the performance of a lab-scale anoxic biotrickling filter. Even though mass transfer constraints and poor solubility of ET were factors, the performance of the biotrickling filter under anoxic settings was superior to that of the bioscrubber and improved the low oxidation rates of ET.

Keywords: volatile organic sulfur compounds; ethanethiol; biotrickling filter; bio-scrubber; electron acceptor; anoxic conditions.

INTRODUCTION

Volatile organic sulfur compounds (VOSCs), including methanethiol (CH_3SH), dimethyl sulfide (CH_3SCH_3), dimethyl disulfide (CH_3SSCH_3), propanethiol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$), butanethiol ($\text{CH}_3(\text{CH}_2)_3\text{SH}$), and ethanethiol (CH_3SH), are widely known to be significant contributors to environmental odor pollution. On the basis of the data in Table 1, VOSCs are characterized by high levels of toxicity, a propensity for corrosion, and exceptionally low olfactory threshold values (for example, 0.01-350 ppbv for ($\text{CH}_3\text{CH}_3\text{SH}$, ET). (Demeestere et al., 2005; Janssen et al., 2013; Sun

et al., 2016; Tangerman, 2009). Toxicity, health concerns, skin, respiratory, and vomiting are some of the symptoms that may result from the exposure to these substances (Giri et al., 2014). In addition, volatile sulfur compounds have a bad smell, toxicity, and corrosive properties. This is why their presence in the atmosphere is undesirable. They are frequently emitted by exhaust gashouse industries. Consequently, they are recognized as being the most complicated air pollution challenges, because of their contribution to ecological and hazardous effect on people well-being causing health problems (Nicell, 2009). Moreover, photochemical smog formation and

Table 1. Chemical and physical characteristics of VOSCs (Janssen et al., 2013; Li et al., 2015; Roman, 2016; Smet et al., 1998; van Leerdam, 2007)

Sulfur compound	Odorant character	B.P. (°C)	M.P. (°C)	OT (ppbv)	H at 25°C	Solubility at 25°C (%)
H ₂ S	Rotten eggs	-60.7	-85.5	8.5–1000	0.41	0.334
CH ₃ SH	Decayed cabbage	6.2	-123.0	0.90–8.5	0.10	2.3
CH ₃ CH ₂ SH	Skunk	35.0	-147.9	0.01–350	0.15	0.676
CH ₃ (CH ₂) ₂ SH	Rotten cabbage, skunk	67.8	-113.1	3.1	0.17	-
(CH ₃) ₂ S	Decayed vegetables	37.3	-98	0.6–40	0.073	2.0
(CH ₃) ₂ S ₂	Irritating putrefaction	109.7	-85	0.1–3.6	0.045	-
(CH ₃ CH ₂) ₂ S	Garlic	92.1	-103.9	0.033	-	-
CS ₂	Sweet ether	46	-112.1	0.21	0.65	0.216
CSO	Pungent	-50	-138.8	-	1.94	0.125

Note: B.P. – boiling point; M.P. – melting point; OT – odor threshold; H – dimensionless Henry coefficient

particulate as secondary pollutants emissions, threatening human welfare and air quality when discharged out into the air (Janssen et al., 2013; Li et al., 2015). The natural sources and anthropogenic sources for emission of (VOSCs) are volcanoes, soil and plants, coastal wetlands, bio-mass burning, ocean, facilities for processing paint and petroleum, landfill gas, liquefied petroleum gas, anaerobic brewery WWTP, synthetic natural gas, factories for rendering, pulp mills, manufacturers of plastics and resins, and chemical industries. They have a crucial role in the chemical interactions of atmospheric aerosols and cloud formation, as well as in the regulation of the global temperature and the circulation of sulfur (Barona et al., 2004; Bentley and Chasteen, 2004; Wu et al., 2018).

The odor emissions from industrial and urban areas have increased people's complaints towards air quality (Badach et al., 2018; Franssen et al., 2002; Pettarin et al., 2015). In order to control odor emissions effectively, the government has passed strict laws and forced businesses to use the right solutions for treating air pollution in order to comply with these laws.

Odor and gas removal technologies have been developed to reduce VOSCs in the environment, and these can be either physical or chemical. The three most common approaches for accomplishing this goal are chemical (chemical scrubbers, thermal oxidation, catalytic oxidation, ozonation, etc.), physical (condensation, adsorption with

activated carbon or clean water scrubbers, etc.), and biological (bio-scrubbers, bio-trickling filters, bio-filters, etc.) (Kennes et al., 1998; Burgess et al., 2001). Physical and chemical procedures have been determined to be the most successful. Nonetheless, secondary pollutants, high costs, and high energy requirements are inescapable. Biological systems such as bio-filters, bio-scrubbers, and bio-trickling filters are highly effective at capturing and removing the waste gases containing volatile organic compounds due to their ease of use and low investment and operating costs (Ak-mirza et al., 2016; Giri et al., 2014). Three primary bioreactor designs have emerged over the years; they are the bio-filter, the bio-scrubber, and the bio-trickling filter. Each type can be distinguished from the other by the use of a carrier material and a mobile liquid phase, respectively (Table 2) (Kennes and Thalasso, 1998).

Bio-filters (attached growth) contain microorganisms in a biofilm form installed on a packed bed consisting of materials such as soil, manure, peat, and synthetic materials or combinations of these (Fig. 1, b), in bio-trickling filters, a layer of inactive filler material is continuously sprayed through a liquid phase spreading from the bottom to the top of the column (Fig. 1c). The principle of bio-scrubbers (suspended growth) is to physically separate gas and liquid phases, and then treat the liquid phase biologically in a bio-reactor. (Fig. 1a) (Dumont, 2015; Mahmood et al., 2007).

Table 2. Important distinctions between the three biological gas-cleaning technologies

Reactor design	Mobile phase	Carrier	Active biomass
Bio-Scrubber	Liquid and gas	None	Dispersed
Trickling bio-filter	Liquid and gas	Synthetic	Fixed
Bio-filter	Gas	Organic / Synthetic	Fixed

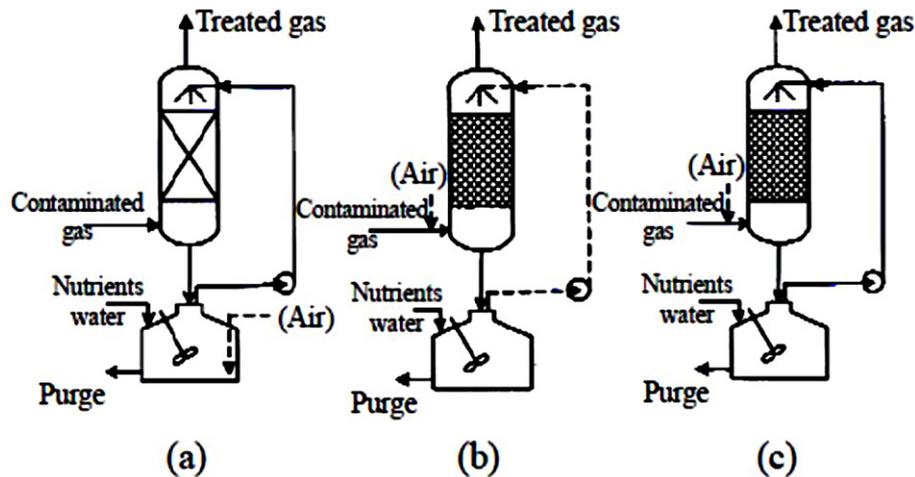


Figure 1. Bioreactors; (a) bio-scrubber; (b) bio-filter; (c) bio-trickling filter

Even though these biotechnological methods for VOSC removal are good, most research has been done on aerobic waste gas treatment, which has higher capital costs for operations (especially energy for pumps or aerators), aeration equipment, and maintenance needs. It may also require monitoring to measure the dissolved oxygen concentration in the liquid (Mahmood et al., 2007). Since there have been relatively few studies evaluating their performance in anaerobic environments, it is clear that bio-treatment alternatives that can effectively treat the VOSCs emissions in these settings are needed to make VOSC processing in the petrochemical industry more environmentally and financially sustainable (Akmirza et al., 2017; Muñoz et al., 2013). In addition to removing nitrogen, anoxic VOSC mineralization by denitrification provides a viable answer for removing VOSC from emissions. Air is not required, and the rate of mass transfer between gases and liquids is unconstrained in anoxic systems since NO_3^- in the liquid medium contains dissolved oxygen. Therefore, anoxic bioprocesses may be desired to counter the limitations of aerobic bioprocesses that include denitrification and VOSC removal (Dumont, 2015). Using NO_3^- to oxidize sulfur compounds has been researched in recent years. Lab-scale batch experiments employing O_2 and NO_3^- as electron receivers were conducted by Yavuz et al. (2007) to examine the removal of sulfide from industrial wastewater. They observed that oxygen removed 80% of sulfide from activated sludge, whereas NO_3^- removed 100%. Denitrifying conditions in a pilot-scale bio-scrubber system were studied in order to convert H_2S in biogas to S^0 or SO_4^{2-} using NO_3^- and nitrite NO_2^- present in feed wastewater. More than 90% of

the H_2S biogas was removed along with nitrogen at a ratio of 2 -to- 3 biogas/wastewater. (Turker et al., 2012). This is in contrast to the typical situation, when nitrogen removal is performed separately from biogas desulfurization, as is the case in most areas where industrial effluent is treated.

To the authors' knowledge, no research has been conducted on anoxic ET biodegradation in waste gas streams. Anoxic mineralization by NO_3^- de-nitrification is a viable platform for removing VOSCs, especially ET from the O_2 -deprived emissions, to yield less damaging by-products, i.e., elemental sulfur. Thus the economic and ecological viability of VOSCs treatment at diverse emission sources can be greatly improved by the development of anoxic bio-trickling filters (attached growth) or anoxic bio-scrubbers (suspended growth), as alternative bio-technologies, which use non- O_2 electron acceptors to oxidize VOCs.

The objective of this work was to assess the bio-degradation capacity of connected and suspended growth systems by filtering ET-laden gas under anaerobic settings in a laboratory using a bio-scrubber (suspended growth) or a bio-trickling filter. Under anoxic circumstances, laboratory-scale bio-scrubbers and bio-trickling filters were utilized to remove the ET gas. Using a restricted NO_3^- source, microorganisms were able to break down ET and convert it to inorganic sulfur, which could then be recovered and used. Additionally, the study set out to investigate how factors like EBRT, concentration of inputs, and spray density impacted the efficiency of bio-process systems at the pilot size. The ET stoichiometric breakdown was designed and tested for various sulfur-based products.

MATERIALS AND PROCEDURES

Experimental design and technological process

Setup of an anoxic bio-trickling filter (ABTF) on a lab scale

The ABTF laboratory scale was made up of a 50 cm transparent Plexiglas column with an internal diameter of 9.4 cm and Kaldness rings (polyethylene, size 14, 9.8 mm², specific surface area > 800 m²/cm³, porosity > 85 percent, and packing density of 0.98 g/cm³) with a working volume of approximately 2 L as well as perforated plates at the bottom and top. Using a peristaltic pump, the feeding tank (diameter 15 cm, height 20 cm) liquid medium (Mineral Salt Medium (MSM) and NaNO₃) was recycled at varying flow rates, counter-current to the gas stream (type PR1 Seko, Italy). Preparation of ET in the gaseous phase was accomplished by injecting the liquid phase into a mixing chamber coupled to a stream of N₂ gas using a dual channel syringe pump (LSP02-1B type, USA). As shown in Figure 2 below, a rotameter (Aalborg Instrument Inc., USA) was used to regulate gas flow in order to achieve the specified empty bed residence time (EBRT) in the laboratory scale version of the ABTF. To speed up anaerobic biodegradation, granular biomass from

an anoxic bio-reactor tank at the Kemberburgaze treatment plant for landfill leachate in Istanbul, Turkey, was added to the packing medium.

Lab-scale of anoxic bio-scrubber setup

Figure 3 depicts the laboratory bio-scrubber system. The bio-scrubber column was composed of cylindrical jacketed PVC (0.10 m inner diameter, 0.5 m height) packed with Kaldness rings (polyethylene, size 14 9.8 mm², specific surface area >800 m²/m³, porosity > 85%, and packing density 0.98 g/cm³) to have a 2 L working capacity (0.25 m height). A perforated sieve supported its bottom and top. The cleaning column was linked to a 3 L bioreactor and magnetically agitated at 400 rpm (biological reactor, manufactured with PVC, 0.15 m inner diameter and 0.2 m height). In the scrubbing column, the polluting gas was converted into the liquid phase, and then sent to the biological reactor, where it was bio-transformed into S⁰ or SO₄²⁻ under anaerobic circumstances, depending on the concentration of NO₃⁻. It was then linked to a sedimentation tank with a working volume of 3 liters (manufactured with PVC, the first part cylindrical with 0.15 m inner diameter x 0.15 m height and second part conical with 0.15 m inner diameter × 0.15 m height). The sedimentation tank effluent

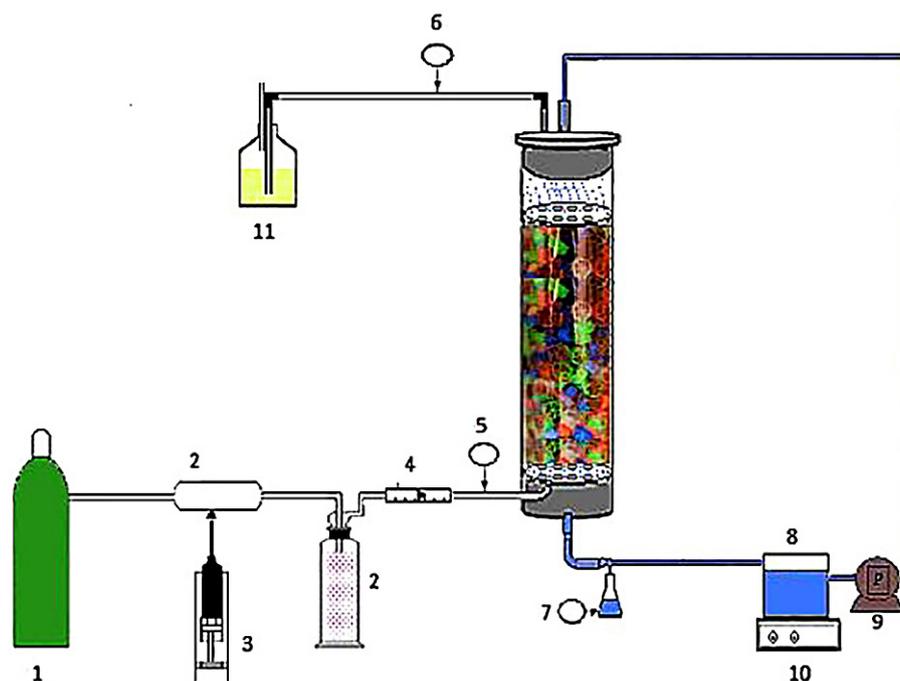


Figure 2. Schematic of an experimental ABTF (1) N₂ gas bottle (3) syringe pump (2) mixing chambers (4) gas flow controller (5) and (6) gas sampling intake and outlet ports (7) liquid sample collection port (8) mineral medium and NO₃⁻ feeding tank (11) NaOH solution (9) recirculation pump (10) magnetic stirrer

was reused in the scrubber. To regulate the flow of sludge and supernatant, peristaltic pumps were used at each connection point. Liquid pollutant was injected into a container containing nitrogen gas (N₂) (Linde Turkey, purity >99.999%) using a syringe pump (MODEL LSP02-1B, Dual Channels Syringe Pump). To produce pure target gas, nitrogen was bubbled into a container as well as allowed to evaporate and condense. After condensation, the gas was mixed with extra nitrogen gas in a separate tank. The negative effects of exhaust gases on the environment led to the addition of

32% NaOH to the bio-effluent scrubber in order to convert the remaining gas to a form that could be easily removed by ET (Frederick et al, 2013).

The gas meter (USA, NY 10962, AALBORG) regulated the flow of synthetic gas into the scrubber and out of it. By means of a water pump, the supernatant was transferred from the sedimentation tank to the bioreactor and then to the settling tank (PR1 peristaltic pump, SEKO Italia S.P.A). The manometer measured the head-loss between the cleaning column intake and outflow to determine how well it converted gas to water.

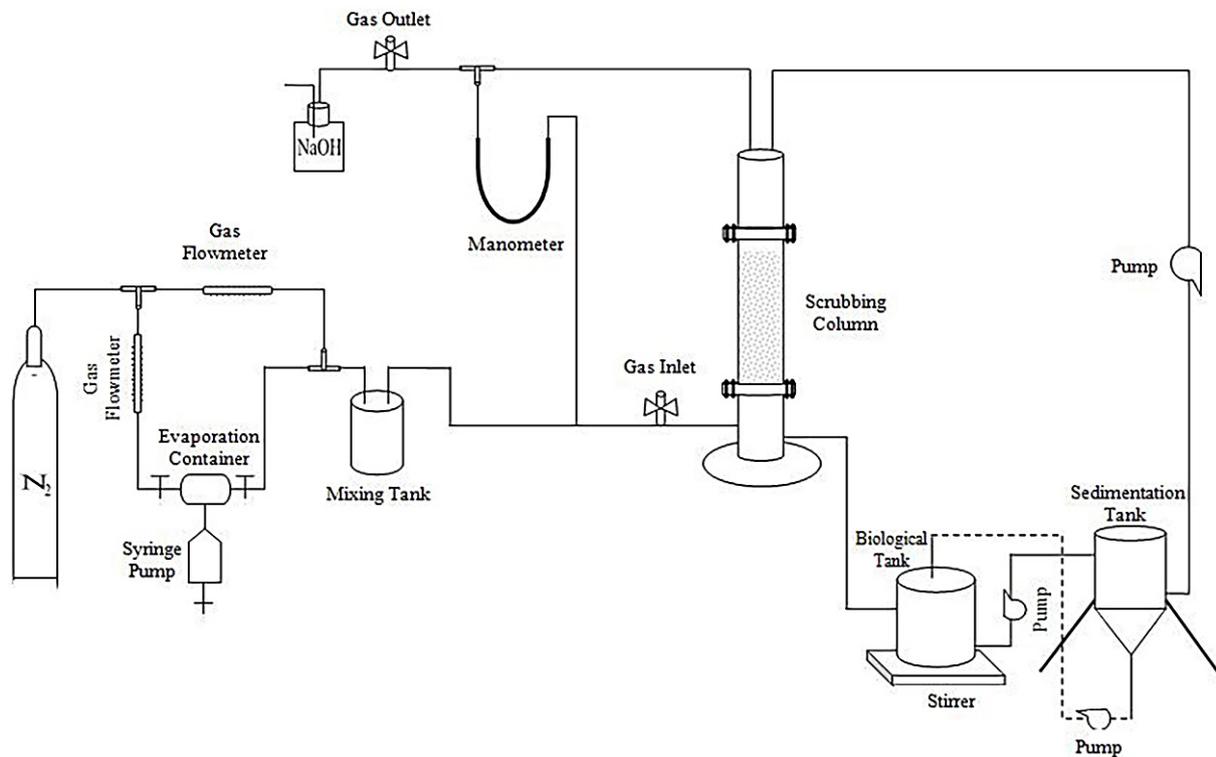


Figure 3. Schematic of the laboratory-scale bioscrubber

Table 3. The experimental settings of a bio-trickling filter and a bio-scrubber on a laboratory scale

Experiments	Target gas inlet concentration (mg/m ³)	EBRT (s)	Gas/Liquid ratio	Irrigation flow rate (mL/min)	Total operation days of all inlet concentrations	Target
E1	88 ± 18 to 1531 ± 150	60	150	14	0–36	Start-up acclimation
E2	150 300 800 1500	60	150	14	36–66	Best G/L ratio
			100	21	67–95	
			80	26	96–121	
			60	35	122–153	
			40	52	154–180	
E3	150 300 800 1500	30	Best gas/liquid ratio	Best irrigation flow rate	181–207	Best EBRT (s)
		60			208–239	
		90			240–272	
		120			273–300	

Laboratory-scale anoxic biotechnologies are necessary to yield maximum RE, thus finding the optimal conditions for them is a priority. Tests were done to evaluate three factors in the bioprocess systems: target gas inlet concentration (ET), gas to liquid ratio G/L, and EBRT, as indicated in Table 3.

Mineral and chemical salt medium

Sigma-Aldrich supplied ET, a chemical with a purity of 99.0 percent. All nutritional mineral salt media (MSM) contained (g/L) $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 6.15; KH_2PO_4 , 1.52; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.2; CaCl_2 , 0.038; and 10 mL/L of a trace element solution containing (g/L) EDTA, 0.5; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.2; $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 0.01; MnC As a chelating agent. Chelation was achieved by adding a diluted solution of ethylenediaminetetraacetic acid (EDTA) to the elemental solution to bind and sequester the metal ions. To ensure that microorganisms had enough nutrients for growth, 30% of the liquid media was replaced weekly with new MSM, and the pH was maintained at a constant 7.2-7.6 throughout all trials by daily renewal of MSM at a pH of 7.0.

To provide an additional electron acceptor in the form of NO_3^- for oxidation of gases and nitrogen for microbial development in a biological tank, a solution of NaNO_3 at a concentration within the range of 5-10 $\text{g}\cdot\text{L}^{-1}$ was created. In addition, NO_3^- was supplied based on the mole ratio of ET to NO_3^- derived from the stoichiometric calculations. Before each experiment began, the YET/ NO_3^- ratio was set to an average of 0.54 between 0.34 and 0.74 whether the final product was sulfate or S^0 , respectively. To ensure sufficient NO_3^- availability at the outset of operations, a 0.54 ET/ NO_3^- ratio was used. NO_3^- consumption rate went up as the duration of operation increased. Therefore, when the final product (S^0 and NO_3^-) was limited, the ET/ NO_3^- ratio was very close to 0.74. In order to keep the experiment in anoxic conditions, the NO_3^- consumption was tracked by an ion chromatograph.

Analytical techniques

A 100L gas-tight syringe equipped with a GC/MS instrument was used to measure the gaseous phase inlet and output concentrations of the scrubbing column and the carbon dioxide of the biologic container (Agilent 5975C-Triple axes with a mass spectrometry detector).

The oven was heated to 40 °C for 3 minutes, then 30 °C/min until it reached 130 °C. Helium gas, flowing at a rate of 1.37 ml/min, was used as the carrier gas. Moreover, effluent and liquid samples were obtained daily from tank's inlet to measure the COD and compound concentrations. The headspace method was used to measure the concentration of aqueous compounds in the recycling liquid at the intake and exit of the bio-biological scrubber's tank to determine its denitrification capacity. Hypovials with liquid samples were heated for 10 minutes at 30 °C. Then, nitrogen gas was forced through the septum into each vial at a pressure of 68.9 kPa. At 0 and 15 and 30 minutes, we gave the hypovials a good shake before replacing them in the water bath. A gas-tight syringe was used to retrieve the 100 L of headspace from the hypovial, and that volume was subsequently pumped into a GMS gas chromatograph (Mundy, 1991). The samples of COD were tested using the open-reflexed (Abawi and Hassan, 1984). A chromatograph equipped with an ICS-3000 was used to determine the concentrations of NO_3^- and SO_4^{2-} throughout the samples of irrigating fluids (DIONEX, USA). The sludge in the biological reactor had its pH measured on a daily basis with the use of a pH-meter (Orion 720 A+, USA). To determine the VSS and TSS, the samples of activated sludge were taken at the conclusion of each investigation and analysed using Methods 2540-E and 2540-D According to Standard Practice. Carbon dioxide (CO_2) concentration was also tested to track microorganisms' ability to absorb carbon during the gas production process.

RESULTS AND DISCUSSION

Operation at startup

To accomplish the required results, the microorganism needed to adjust to the odorous waste gas up until a stable state was reached, i.e. the concentrations of inlet and outlet gases were constant. For 36 days, an ET inlet concentration starting of 8818 mg/m^3 to 1531150 mg/m^3 , a G/L ratio of 150, and an EBRT time of 60 seconds were passed through the employed lab-scale biotrickling filter and bioscrubber (see Fig. 1). Then, portion of the odorous ET gas was injected into both columns. A high RE of 88% can be attributed to the intense competition amongst microbes for the available organic substrate (ET). Due to the

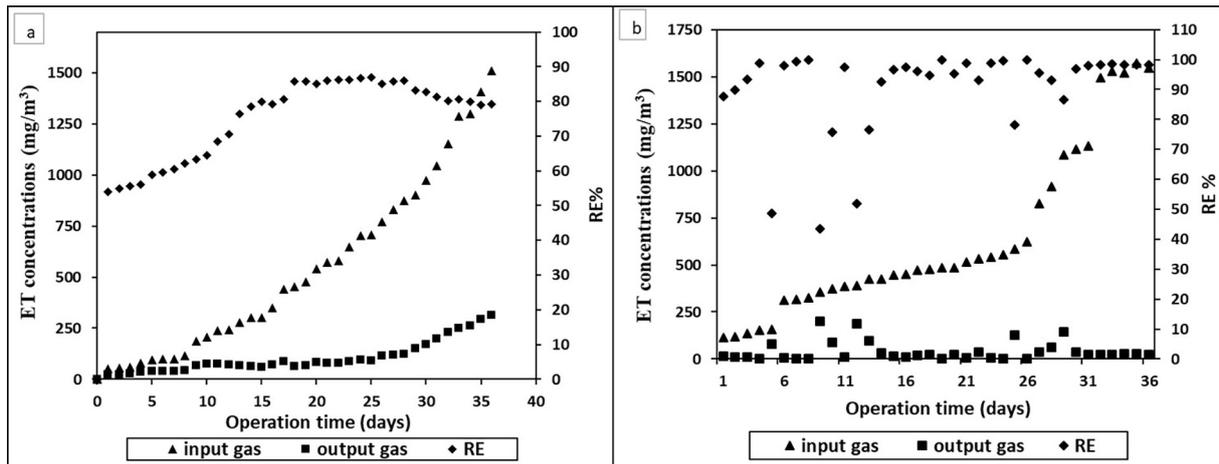


Figure 4. Start-up performance of a biotrickling filter (a) and a bioscrubber (b) (▲ ET concentration at input ■ ET Concentration at Output ◆ Efficiency of removal)

microorganisms' adaptation to the treated gas, the concentration of the inlet gas was gradually increased, reaching a maximum of 1531 150 mg/m³. However, from the 19th to the 28th day of constant running, the bioscrubber performance was stabilized at an average of 86 percent with higher concentrations of 469-875 mg.m⁻³ at the intake of the ET. The RE then started to drop, eventually reaching 79% after eight days of continuously irrigating the system with ET concentrations as high as 900 mg/m³. As can be shown in Figure 4, stability was achieved in the output concentrations after 36 days of operation (a-b).

RE and EC affected by G/L and inflow concentration

Hydrophilicity of ET gas is on the moderate side, with a Henry constant of (0.15-0.2) (Wang et al., 2015). The gas-to-liquid flow rate, denoted by the symbol G/L, has been shown to be a crucial characteristic in all known biological desulfurization processes (Fortuny et al., 2011). Optimal values must be determined experimentally and case-by-case. Removal efficiency (RE) and elimination capacity (EC) at EBRT were analyzed as a function of five different G/L ratios (40, 60, 80, 100, and 150) as shown in Fig. 5(a-d) (60 sec). When the G/L ratio was lowered from 150 to 40, the RE for the biotrickling filter rose from 62.5 to 80.6 percent and the bio scrubber rose from 71 to 76% when exposed to extremely high concentrations of ET (1500 mg/m³). In both systems, the EC rose from 58 to 75 g/m³ hr. and, more modestly, from 62 to 66 g/m³ hr. This pattern in ET breakdown is linked to microbial requirements,

such as the amount of nutritional solution needed for normal metabolism and growth (Hernández et al., 2012). Since this is the case, the metabolic rate of the microbe can be controlled by the availability of nutrients in the nutrition solution. When the liquid flow rate is increased (the G/L ratio is decreased), more nutrients and oxygen supply (in the form of NaNO₃) are available to the microbe, which speeds up its metabolic activity and accelerates ET degradation.

ET REs were shown to decrease with increasing inflow concentration across the board, while EC REs were found to grow in the opposite direction. Therefore, this work shows how the concentrations of ET at the intake and the G/L ratio affect RE and EC when the concentrations of ET are 150, 300, 800, and 1500 mg.m⁻³. At low ET inflow concentration, i.e. 150 mg/m³ and G/L ratio of 150, the RE for biotrickling filter was 78.6% (EC = 7.3 g/m³ hr) and for bioscrubber it was 85.0% (EC = 7.6 g/m³ hr). When the ET intake concentrations were increased by a factor of 10, from 150 mg/m³ to 1500 mg/m³, the removal efficiency (RE) of the biotrickling filter dropped to 62.5 (EC = 58.1 g/m³ hr), while the removal efficiency (RE) of the bioscrubber rose to 71% (EC = 62 g/m³ hr). There was a marked improvement in performance between the biotrickling filter and the bioscrubber system at a G/L ratio of 40. RE decreased from 92.3 to 80.6% (EC from 7.5 to 75 g/m³ hr) in biotrickling filter and bioscrubber system, respectively. Because of the large sprinkling amounts of the irrigated liquid, the biomass loss from packing rings may be to blame for the decrease in RE, and the low solubility of ET in

water may explain the shorter hydraulic retention time (Salamanca et al., 2017; Wan et al., 2011).

Moreover, the decrease in the liquid flowrate was credited by Potivichayanon et al. (2006) as the cause of the drop in the RE and EC of ET, as it assisted to minimize the mass transfer rate between the gas and liquid. There were two distinct patterns of inflow concentration behavior. Diffusion limitation was the primary regulating factor at low ET doses (150 and 300 mg/m³). As ET concentrations were kept low (In the range of 150–300 mg/m³), diffusion limitation served as the primary regulating process. At high ET concentrations (800 and 1500 mg/m³), there was less of a problem with diffusion because the concentration of gas differences was going up. The poor solubility effect of ET can therefore be mitigated by the gas liquid mass transfer flux, which is proportional to the gas concentration's gradient.

A rise in fertilizer irrigation will grow biomass and create bio surfactants, both of which enhance the efficacy of this method (Kraakman et al., 2011). Both systems, when the G/L ratio is raised to 80, can obtain a RE of 90.8% even when exposed to an inlet concentration of ET as low as

150 mg/m³. To significantly affect RE and EC at a higher ET inflow concentration (i.e. 1500 mg/m³), the G/L ratio must be reduced to 40 and 80, respectively (approximately 80.6% and 75 g/m³ hr. for biotrickling filter and 75.8%, 66.2 g/m³ hr. for bioscrubber). Therefore, the decrease in RE that occurs at ever-increasing inflow concentrations in the scrubber column is attributable to the fact that, while higher inlet loads lead to greater ET absorption, at these loads, the possible inhibition of substances in a liquid bioreactor tank slows down biological activity, which lowers RE (Rappert & Müller, 2005). After this point, the spray density was increased, but the REs barely budged, since the ET had essentially reached its maximum capacity, Water was only moderately soluble (0.15–0.21 for Henry's dimensionless coefficient) and the dense biomass in the bio-tank may have slowed ET gas transport. Therefore, the microorganisms were probably recycled through the irrigation system after failing to breakdown ET completely. In contrast, the HRT decreased from 2 hours at a G/L ratio of 80 to 1.4 hours at a G/L ratio of 60 and 1 hour at a G/L ratio of 40 as the spray density increased. Therefore, it stands to reason that if the time it takes for ET

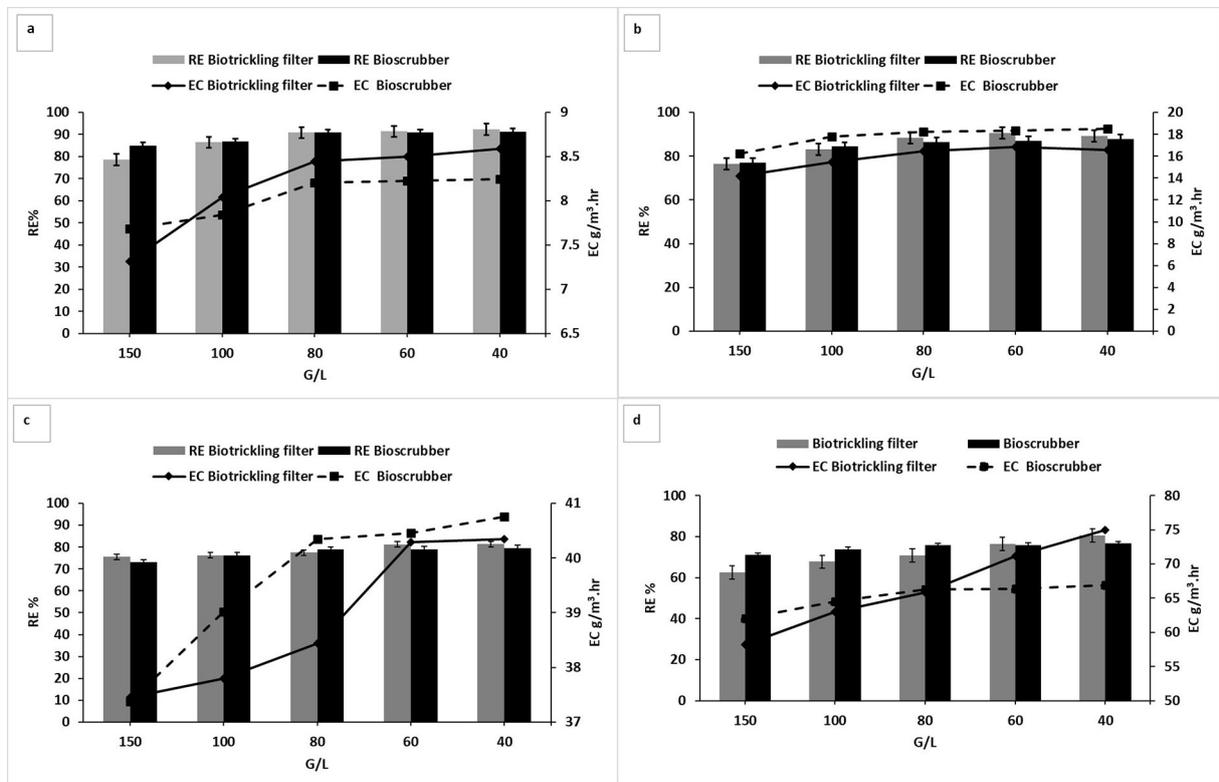


Figure 5. The effect of G/L ratio on the efficiency and capacity with which ET is removed at different intake concentrations (150 (a), 300 (b), 800 (c), and 1500 (d) mg/m³). Standard deviations (SDs) of replicate samples are shown as error bars

to biodegrade in a biological tank is cut down, some of the ET that has not been completely broken down will return into the water used for irrigation. In a prior study, increasing the liquid to gas ratio (L/G) from 0.001 to 0.005 (irrigation velocity 0.22–1.13 m/h) increased H₂S RE from 88.5% to 99.7%. (Chen et al., 2006). At an input H₂S concentration of 40 ppm and an EBRT of 45 s, Abdehagh et al. (2011) observed that the RE of H₂S increased from 85.0 to 100.0% when the rate of liquid recycling was raised from 0.46 to 0.92 m/h. Nevertheless, it is possible that higher concentrations of ET inflow during operation led to more biomass building up in the biological reactor, where ILs ranged from 9.32 to 87.10 g/m³ hour. After every six days, the biomass concentration in the biological reactor rose by 30% (measured in VSS mg/L). Previous studies on spray density and ET removal from a bio-trickling filter showed that increasing the spray density to 0.24 m³/m² h significantly improved the REs of three ET concentration groups (110, 200, and 300 mg/m³), with RE values of about 60% being reached. Additionally, a consistent RE trend was found in all three groups when the density of the spray exceeds 0.24 m³/m² per hour. This was because as

the surface of the packing material became wetter, the biomass grew too thick. This made it hard for the ET molecules to infiltrate into microorganisms and slowed down the breakdown of ET (Wang et al., 2015). The obtained results outperformed those of An et al. (2010) with aerobic biotrickling filters, the overall elimination capacity increased from (13.64 g.m⁻³.h) to (34.23 g.m⁻³.h) as the ET inlet concentration rose from (0.42 to 1.05 mg.L⁻¹). For the bioscrubber, the optimal G/L ratio was 80 (HRT = 2 h), while the optimal G/L ratio for the biotrickling filter was 40.

Influence of EBRT and intake concentration on RE and EC

Time to reach the concentration limit is a good measure of the effect EBRT has on any biotreatment desulphurization process (Pokorna et al., 2015). Analysis of the effects of EBRT on reactive oxygen species (RE) and elemental carbon (EC) at four different inflow concentrations. At a constant G/L ratio of 40, the treatability performance of the biotrickling filter and bioscrubber was evaluated throughout four EBRT intervals (30, 60, 90, and 120 sec) (Fig. 6(a-d)). Raising the EBRT resulted in a proportional increase

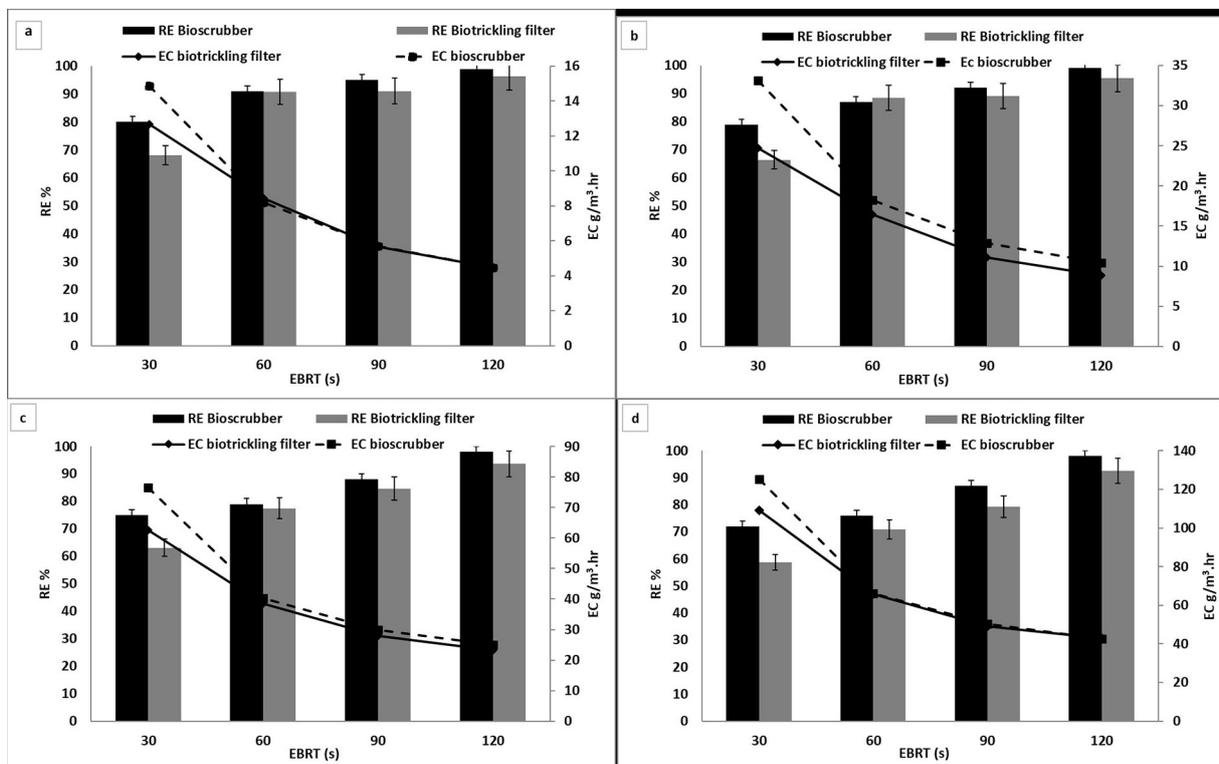


Figure 6. The effect of different input concentrations (150 (a), 300 (b), 800 (c), and 1500 (d) mg/m³) on EBRT efficiency and capacity for eliminating ET (d). Sample standard deviations are shown as error bars

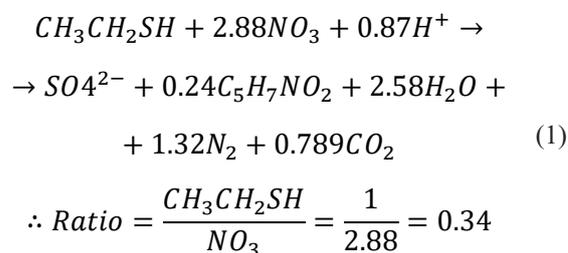
in RE, but increasing the EBRT from 30 to 60 seconds resulted in a striking rise in RE in the biotrickling filter, from 68.2 to 90.8% (maximum EC was lowered from 12.6 down to 9.1 g/m³·hr) at ET inlet concentration 150 mg/m³. Increases in EBRT time of up to 120 seconds were required at concentrations of 1500 mg/m³ to obtain a RE of 92.6% (highest EC of 42.6% per cubic metre per hour). There was, however, no discernible change when the EBRT time was doubled from 60 to 120 seconds. Under high ET input concentrations of 1500 mg/m³ for 60 and 120 sec, the RE scarcely rose, from 80% to 86%. The relative effectiveness (RE) remained relatively unchanged from 60 to 120 seconds of EBRT at low ET inlet concentrations, remaining about 92% at concentrations of 150 mg/m³. According to the findings, boosting the EBRT for up to 60 seconds is sufficient to boost the removal efficiency of the biotrickling filter. From a different perspective, the effect of EBRT on RE and EC in bioscrubber revealed that high RE values were comparable (at roughly 99%) at ET concentrations of 150 and 300 mg/m³ and at ET concentrations of 800 and 1500 mg/m³ (at about 98%) with EBRT of 120 s. Using a shorter EBRT pulse duration of 30 s, the highest EC values for 150, 300, 800, and 1500 mg/m³ were 14.40, 33.10, 76.50, and 125.28 g/m³·h, respectively. The average ECs were 24.74 and 20.60 g/m³·h at an EBRT of 90 and 120 s, respectively, and the high REs were roughly 91 and 99 percent for the four inlet concentrations. Therefore, for a G/L ratio of 80, ET treatment for 90 seconds in an anaerobic bioscrubber system constitutes the optimal EBRT, as determined by REs and ECs.

When comparing the results of this study to those of others, it is clear that anoxic circumstances, a mixed culture, and the lack of biomass species selectivity all contribute to significantly increased ET RE and EC, while simultaneously decreasing EBRT. To purify ET in an aerobic environment, An et al. (2010) used a mixture of microorganisms seeded in twin bio-trickling filter columns to achieve ECs of 38.36 g/m³·h with 89.2% RE and 25.8 g/m³·h with 57.1% RE, respectively, after 83 seconds of EBRT. In another work, the maximum EC was only 3.7 g/m³·h with a RE of 50% for ET at an EBRT of 40 s in an aerobic biotrickling filter infected with alkaliphilic sulfo-oxidizing bacteria under alkaline conditions (ArellanoGarca et al., 2010; ArellanoGarca et al., 2011).

Growth stoichiometry and sulfate production

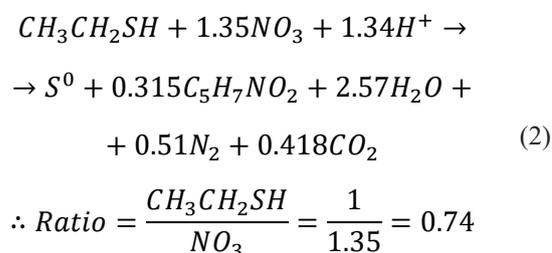
Microorganisms obtain energy by using an electron acceptor (an oxygen molecule) to oxidize their food source. (Baspinar et al., 2011). Under anaerobic (anoxic) circumstances, nitrate, sulfate, and carbon dioxide are employed as electron acceptors in the energy metabolism of all microorganisms that are not photosynthetic. The most efficient way to make energetic reactions, especially complicated ones like ET, is to use the half-reaction method.

On the basis of the authors' prior work, the following stoichiometric equations were developed via thermodynamic analysis (Mhemid et al., 2019; Shihab et al., 2018). Stoichiometric analysis of the ET reaction leading to sulfate as the major product:



where: $\Delta G = -1389.26$ kJ/e-mole.

ET stoichiometric process with elemental sulfur as the primary product:



where: $\Delta G = -674$.

By adjusting the S/N molar ratio, it is possible to regulate the oxidation level, or the desulfurization byproducts. According to the research on the removal of sulfide and nitrate in wastewater (Baspinar et al., 2011; Doan et al., 2012; Turker et al., 2012), the S/N molar ratio has a significant impact on the degradation products. It's possible that the effect will not be the same as in other settings because eliminating biogas involves mass transfer from gas to liquid, followed by absorption/adsorption, and then biodegradation. As far as the authors know, no studies have looked at how S/N ratios affect the removal of ET gas and byproducts of desulfurization in anaerobic environments. Table 4 displays the data from

experiments that fall within the theoretical scale. The value ranges between 0.34 and 0.74 mole ET/mole of NO₃⁻. Table 1 demonstrates that as ET inflow concentration rose from 15034 to 1500120 mg/m³, nitrate consumption also increased. This discovery suggests that biomass can enhance denitrification efficacy due to its high biodegradation potential for dealing with odorous gas at high loading rates. Additionally, the data distribution of most final products is shown in Fig. 7 (a-b), which reveals that sulfate and elemental sulfur were frequently discovered together. This demonstrates that the production of elemental sulfur occurred simultaneously with that of sulfate. In 2016, Li et al. looked at how changing the S/N ratio affected the efficiency with which a biotrickling filter (BTF) and a bubble column removed H₂S from biogas (BC). The BTF's H₂S removal performance was more stable than that of BBC because of changes in how mass moved between gases and liquids. For S/N ratios between 1 and 2.5, the maximum EC of H₂S was 54.5 g H₂S/m³h, indicating that biotrickling filters were able to effectively remove nearly all of the gas. Although the efficiency of desulfurizing biogas was not

considerably impacted by S/N ratios, the products of desulfurization were. As the S/N ratios increased from 1.0 to 2.5, denitrification performance increased and SO₄²⁻ concentrations dropped. Baspinar et al. (2011) found that more than 95% of H₂S was removed from biogas using a molar ratio of H₂S/NO₃⁻ between 0.72 and 2.89 in a pilot-scale absorption tower.

In the absence of sufficient amounts of NO₃⁻, Table 4 shows that S⁰ is produced as a byproduct. Systems in which S⁰ is formed as the major product reduce both NO₃⁻ consumption and biomass output compared to systems in which SO₄²⁻ is formed as the main product. When ET is oxidized in the absence of oxygen, it produces SO₄²⁻ and S⁰ with respective activation energies of 1398.88 and 675.73 kJ/e-mole and 675.73 kJ/e-mole, respectively. This negative signal points to an exothermic, naturally occurring process. Yield molar ratios (Y_{ET/NO₃⁻}) from Table 4 are shown, along with their theoretical upper and lower limits in Figure 7 (a-b). The majority of experimental molar ratios were within the theoretical range (0.35-0.74), and elemental sulfur was the dominant final product (Fig. 7a & b). These findings are discussed in terms of the

Table 4. The yield ratios of both systems, as measured experimentally and predicted theoretically

Inlet concentration mg/m ³	G/L ratio	Biotrickling filter			Bioscrubber			Thermodynamically Y _{ET/NO₃⁻} (mol/mol) Main product S ⁰ SO ₄ ²⁻	
		Average ET removal gr/day	Average NO ₃ ⁻ Consumption gr/day	Experimental Y _{ET/NO₃⁻} mol/mol	Average ET removal gr/day	Average NO ₃ ⁻ Consumption gr/day	Experimental Y _{ET/NO₃⁻} mol/mol		
150±34	150	0.36	0.49	0.73	0.25	0.31	0.8	0.74 0.35	
300±55		1.2	2.13	0.56	0.54	0.75	0.72		
800±74		1.98	3.39	0.58	1.38	2.4	0.58		
1500±120		2.72	4.14	0.6	2.1	3.4	0.62		
		Average ±SD 0.62±0.06			Average ±SD 0.51±0.10				
150±34	100	0.41	0.8	0.51	0.26	0.37	0.7		
300±55		0.91	2.45	0.37	0.6	0.8	0.75		
800±74		2.14	3.54	0.66	1.33	1.91	0.7		
1500±120		2.34	5.56	0.42	2.14	3.54	0.6		
		Average ±SD 0.49±0.10			Average ±SD 0.63±0.16				
150±34	80	0.38	0.76	0.50	0.27	0.44	0.61		
300±55		0.93	3.2	0.29	0.59	0.9	0.66		
800±74		2.02	2.91	0.69	1.34	1.94	0.69		
1500±120		3.2	6.37	0.5	2.19	3.9	0.56		
		Average ±SD 0.50±0.14			Average ±SD 0.6±0.17				
150±34	60	0.31	0.61	0.51	0.28	0.43	0.65		
300±55		0.87	2.57	0.34	0.61	1.18	0.52		
800±74		1.85	3.07	0.6	1.36	1.87	0.72		
1500±120		3.61	6.13	0.58	2.2	4.75	0.46		
		Average ±SD 0.51±0.10			Average ±SD 0.67±0.050				
150±34	40	0.37	0.71	0.52	0.27	0.73	0.37		
300±55		0.79	2.85	0.28	0.64	1.93	0.33		
800±74		2.0	4.7	0.42	1.38	2.4	0.58		
1500±120		4.14	7.74	0.53	2.22	5.22	0.43		
		Average ±SD 0.43±0.10			Average ±SD 0.53±0.08				

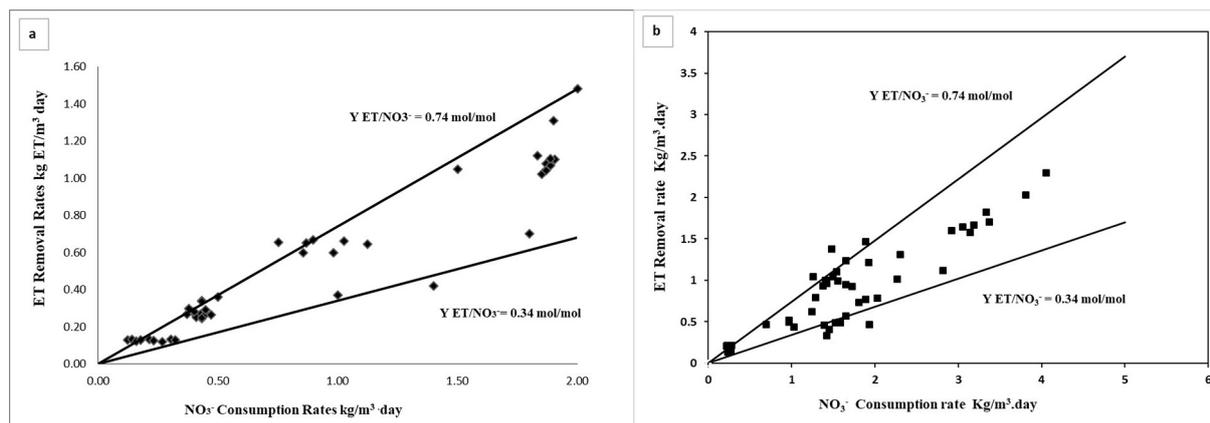


Figure 7. Biotrickling filter (a) and bioscrubber (b) ET/NO₃ molar ratio, experimental against theoretical yield (b)

existence of S⁰. The conducted calculations show that the average experimental yields for Y_{ET/NO₃}, where S⁰ is the main product, are close to the value of 0.74 that was predicted.

This shows that S⁰ was made in both systems by a combination of S⁰ and other sulfur compounds and not by the formation of SO₄²⁻. First, S⁰ is insoluble and hence easy to remove; second, S⁰ may be recovered and used as a valuable raw material (for example, in bio leaching processes in sulfuric acid production facilities after purification from the water stream by gravity sedimentation, such as in a named plate settler; and third, as more oxygen is required to produce SO₄²⁻, a larger energy consumption is thus required for aeration, making the S⁰ creation the preferable option (Janssen et al., 2013). Separating S⁰ from the water flow can be done in a variety of ways, including using settlers, filter presses, or sulfur melters, and the method chosen depends on the required purity of sulfur elements. (Pagella et al., 1996). Thus, in our functional system, the biotrickling filter and bio-scrubber biomass can be transferred to the vacuum filter press to recover the S⁰.

CONCLUSIONS

Under anoxic circumstances, the lab-scale biotrickling filter operation with nitrate as the electron acceptor outperformed the bioscrubber system. Instead, the anoxic biotrickling filter in the laboratory performed better. With the optimal operating circumstances, the ET removal effectiveness was better than 90.8% at a G/L ratio of 80 for an input concentration of 150 mg/m³, but it declined to 80.6% at an inlet

concentration of 1500 mg/m³ while maintaining the same EBRT time constant (60 s) and emission concentration maximum (75.18 g/m³.h). Inlet concentration of 150 mg/m³, gas-to-liquid ratio of 80, and equivalent biological retention time (EBRT) of 90 seconds yielded the optimal operating parameters and operation characteristics for the bioscrubber. The maximum EC was determined to be around 50 g/m³.h at inlet ET values of 1500 mg/m³. The average RE was found to be 91%. The elimination effectiveness of ET was unaffected by changes in G/L ratio greater than 80 at any of the tested concentrations. The average yields from experiments using nitrate as the electron acceptor agreed well with the stoichiometric formulae and thermodynamic estimates produced from these reactions. The result was more in line with the theoretical value (Y_{ET/NO₃}) of 0.74 when S⁰ was the primary product, implying that S⁰ and other sulfur forms were generated rather than SO₄²⁻.

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