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Study on the Performance of an Anoxic Biotrickling Filter for the Removal of Hydrogen Sulphide from Biogas

Gabriela Soreanu, Patricia Falletta,* Michel Béland, Kara Edmonson, and Peter Seto

Environment Canada, Aquatic Ecosystems Management Research Division, 867 Lakeshore Road, Burlington, Ontario L7R 4A6, Canada

The paper presents aspects related to the performance of an anoxic biotrickling filter designed for hydrogen sulphide (H_2S) removal from biogas. In this process, nitrate was supplied through a nutrient solution as an electron acceptor for anoxic growth of H_2S-oxydizing microorganisms. The biotrickling filter's packing media consisted of a layer of plastic fibres over volcanic rocks in a ratio 0.78:1 by volume. The total volume of packing media was 0.014 m^3. Several H_2S loading rates (IL) were tested under continuous dynamic conditions, ranging between 20 and 550 g of H_2S feed/(m^3bed·day). Maximum process performance (>95%) was observed for IL ranging up to approximately 300 g of H_2S feed/(m^3bed·day). The degradation of hydrogen sulphide occurred with the formation of both sulphate and elemental sulphur, their formation ratio being dependent on H_2S loading rate. Elemental sulphur was found to be the dominant degradation product, particularly at IL > 96.18 g of H_2S feed/(m^3bed·day). The use of two biotrickling filters in series was also tested, and a significant improvement in process performance was observed. This technology allows simple operation with low maintenance and has the potential for sulphur recovery.

Key words: **anoxic, biofiltration, biogas, biotrickling, denitrification, hydrogen sulphide**

Introduction

Hydrogen sulphide (H_2S) in biogas represents an environmental and safety concern, and its presence in fuels may cause technical problems in the operation of engines (Syed et al. 2006). Due to these aspects, hydrogen sulphide is recognised as a significant barrier in anaerobic digester biogas utilization at municipal sewage treatment plant facilities (Soreanu et al. 2005). Hydrogen sulphide is listed as one of the top five substances released to the environment in Canada as reported in the National Pollutant Release Inventory (NPRI 2002) administered by Environment Canada. While expensive conventional physical-chemical technologies for H_2S removal from gas fluxes are available (Syed et al. 2006), recent studies show that hydrogen sulphide in biogas can be removed in cost-effective anoxic biological systems by denitrifying bacteria (Soreanu et al. 2007, 2008). For example, *Thiobacillus denitrificans* can metabolize inorganic compounds, such as hydrogen sulphide under anoxic conditions, when nitrate is used as an electron acceptor (Tiedje 1988; Prescott et al. 2002). The process does not affect the methane content in biogas. While nitrate was found to be more efficient in biological H_2S removal, nitrite was shown to sustain the biological process at a lower performance. Other aspects related to this process, including microbiological investigations, influence of individual operational parameters, and kinetic and degradation rates (etc.), are presented in Soreanu et al. (2007, 2008). Some aspects related to the cost benefits and environmental significance of implementing such a technology in the municipal or industrial sector are also presented in Soreanu et al. (2008).

The present study confirms the previously reported results and shows that the denitrifying microorganisms are developed under specific environmental conditions, which are important in the management and start-up of the biotrickling filter. The influence of H_2S loading rate on the process performance and the degradation pathway are presented in the present study, as well as other technical aspects such as the use of two biotrickling filters in series for performance enhancement and sulphur recovery.

Material and Methods

Experimental Installation

The experimental installation (Fig. 1) consisted of a biotrickling filter made from a 15-cm diameter polyvinyl chloride column. The column was packed with media consisting of an upper bed of plastic fibre layers (2-cm thickness; 0.1- to 0.2-mm fibre diameter) and a lower bed of volcanic rock (1- to 2.5-cm diameter) in a ratio of 0.78:1 by volume. The total height of the packing media was 0.8 m and the corresponding total volume was 0.014 m^3. The packing media was pre-inoculated with a nutrient solution from another anoxic biotrickling filter treating hydrogen sulphide in biogas. The biogas containing hydrogen sulphide was continuously fed at the bottom of the column, while the nutrient solution was continuously fed at the top, countercurrent to the direction of the gas stream. The biogas was generated by a pilot-scale anaerobic digester treating municipal organic waste from Toronto, Ontario, Canada. The nitrified

* Corresponding author: Pat.Falletta@ec.gc.ca

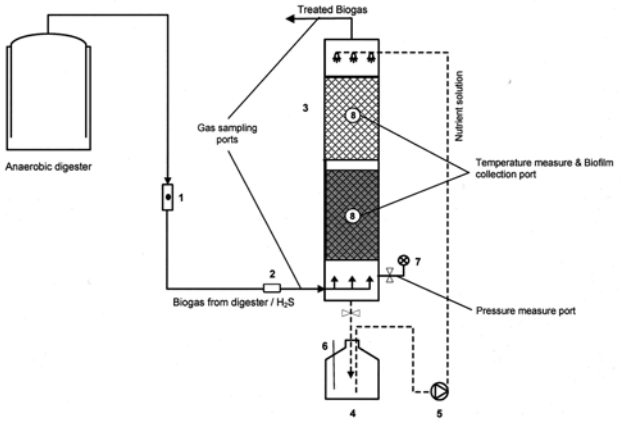

Fig. 1. Experimental installation set-up. 1: gas flowmeter; 2: gas equalization bottle; 3: biotrickling filter (packing bed dimension: 15-cm diameter; 0.8-m total height; 0.014-m^3 total volume); 4: nutrient solution tank; 5: peristaltic pump; 6: pH electrode; 7: manometer; 8: thermocouple. Open hatching: plastic fibre (0.35 m media height); shaded hatching: volcanic rocks (0.45 m media height).

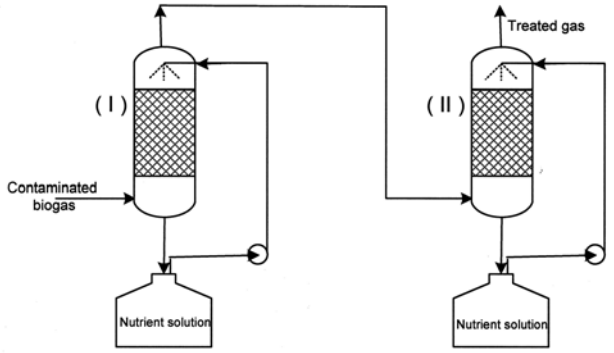

Fig. 2. Simplified diagram of two bioreactors operating in series.(I): Biotrickling filter packed with plastic fibres (0.012 m^3); (II): Biotrickling filter packed with plastic fibres and volcanic rocks (0.014 m^3). Hatched area, packing bed: (I), 0.68-m media height; (II), 0.80-m media height.

effluent from a pilot-scale sequencing batch reactor treating municipal sewage on site was used as the source of nutrient solution. Additionally, the H_2S concentration in the biogas was supplemented, when required, using a H_2S generation unit. The biogas and the nutrient solution flowrates were measured using a flowmeter (Cole-Parmer, Model PMRI-010296) and an auto-control peristaltic pump (MasterFlex, Model 77200-62), respectively.

Figure 2 shows the simplified diagram of the experimental installation used for the testing of two bioreactors in series. The second reactor in this set-up was identical to the reactor shown in Fig. 1, while the first reactor contained 0.012 m^3 of plastic fibres (versus 0.014 m^3 of plastic fibres and volcanic rocks in the second reactor). The output biogas flux exiting from the top of the first reactor was fed to the second reactor at the bottom.

Nutrient Solution

The nitrate rich nutrient solution was prepared according to Soreanu et al. (2008). Sodium nitrate ($NaNO_3$) was added in excess in order to raise the initial concentration to 1,400 mg of $N\text{-}NO_3^-$ per litre, and thus assure nitrate nonlimiting conditions for long-term testing under variable H_2S loading rates. After an initial pH adjustment of the nutrient solution to approximately 6.5 (Soreanu et al. 2008), the pH was itself maintained in the range of 5.8 to 6.3 over the course of the test period. Composition of the nutrient solution was recorded daily. During each experiment, the nutrient solution composition varied due to the nitrate consumption and the formation of the degradation products, however nitrate concentration remained in excess over stoichiometric conditions (Soreanu et al. 2008). The standard deviation of the nutrient solution for the analyzed compounds (presented below) in the samples collected at the same time was less than 5%.

Analytical / Measurements Methods

A gas chromatograph equipped with a thermal conductivity detector (GC/TCD, Agilent 3000A, model G280) was coupled to gas sampling ports located before and after the bioreactor, in order to perform the analysis of biogas for H_2S, CH_4, CO_2, O_2, and N_2 (Soreanu et al. 2008). The nutrient solution was analyzed for $N\text{-}NO_3^-$, $N\text{-}NO_2^-$, $N\text{-}NH_4^+$, SO_4^{2-}, and $S_2O_3^{2-}$, according to Standard Methods for the Examination of Water and Wastewater 21st Edition (APHA et al. 2005), using a Dionex ICS 2000 Ion Chromatograph (Method 4110B) and Technicon TRAACS Autoanalyser (Method 4500-NH_3 G), respectively, as described in Soreanu et al. (2008). Characterization of the solid material collected from the packing media was performed. Additionally, sulphur, iron, and sodium were extracted from the solid samples using a modified Standard Method 3050 B and analyzed via an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer OPTIMA 5300DV) according to Method 6010 B (U.S. EPA SW-846 1996). The pH of the nutrient solution was monitored continuously with an immersed Orion pH electrode (model 912600) coupled to a digital pH controller (ETATRON DS, model PBX0922110bA). The packing bed temperature and the pressure drop across the biofilter were measured as described in Soreanu et al. (2008).

Traces of $S_2O_3^{2-}$ and $N\text{-}NH_4^+$ were rarely detected in the nutrient solution, thus reference to their presence is neglected in further discussions. Nitrogen could not be

accurately analyzed during the study due to its very small concentration (a mass balance was instead adopted). The temperature gradient and change in pressure across the biofilter were insignificant and are not discussed further.

Experimental Methodology

Experiments were carried out under dynamic conditions for approximately 2 months, where the microorganisms' acclimatisation time was approximately 5 to 6 days, and the time frame of each test was 3 to 4 days. Over the course of the test period, the biogas was fed continuously at the bottom of the column and the nutrient solution at the top, counter-current to the gas flow, at a constant nutrient solution flow rate of 30 L/h. The influence of H_2S loading rate on process performance and on the degradation pathway was investigated under nonlimiting nitrate conditions. H_2S loading rate was increased gradually between 24.05 and 543.96 g of H_2S feed/(m^3bed·day), by varying the biogas flow rate and H_2S concentration, while the corresponding gas contact time varied between 12 and 85 minutes. The criteria used for the estimation of process performance were H_2S removal efficiency (RE, %), H_2S loading rate [IL, g of H_2S feed/(m^3bed·day); or IL', g of H_2S feed per day], elimination capacity [EC, g of H_2S removed/(m^3bed·day); or EC', g of H_2S removed per day] and nitrate demand (g of $N\text{-}NO_3^-$ consumed per g of H_2S removed). The formulas for determining these criteria are presented in Soreanu et al. (2008). Theoretical reactions describing possible degradation pathways for hydrogen sulphide oxidation to elemental sulphur and sulphate based on nitrate reduction to nitrite and nitrogen are presented in Soreanu et al. (2008). Hydrogen sulphide, nitrate, sulphate, and nitrite, were quantitatively analyzed in the present study, while elemental sulphur and nitrogen were calculated from the corresponding mass balance.

Result and Discussion

Influence of the H_2S Loading Rate (IL)

Figure 3 presents H_2S removal efficiency (RE) and the corresponding reactor elimination capacity (EC) under different H_2S loading rate (IL) conditions over 30 days of operation. A series of tests were undertaken at different H_2S loading rates. For each H_2S loading rate, the test was maintained at steady-state for a period of at least 2 days, and the corresponding EC was observed. After each test, the level of H_2S was returned to the normal level found in the pilot-scale digester biogas used for this set of experiments.

After the initial start-up of the biotrickling filter, a short acclimatisation period of 4 days (day 0 to 4) was required in order for the bioreactor to reach maximum performance (RE = 100%) (Fig. 3).

As can be observed in Fig. 3, the increase of EC is directly proportional to the increase of IL up to approximately 300 g of H_2S/(m^3bed·day), and a maximum process performance (RE = 95 to 100%) was recorded as well. When the IL was increased further, no significant improvement in EC was observed, and therefore the RE decreased, [i.e., down to 70.71% for an IL of 543.96 g of H_2S/(m^3bed·day)]. The decrease in the RE could be mainly attributed to the limited mass transfer between the phases involved in the process (biogas, nutrient solution, biofilm) as a result of their insufficient contact time due to the high IL, as also explained in Soreanu et al. (2007) and Devinny et al. (1999). Increasing the contact time by increasing the packing volume showed significant improvement in process performance as described later in this paper. Other authors (McComas and Sublette 2001; Kim et al. 2002) reported the possible inhibition of biological process by high IL and elemental sulphur accumulation.

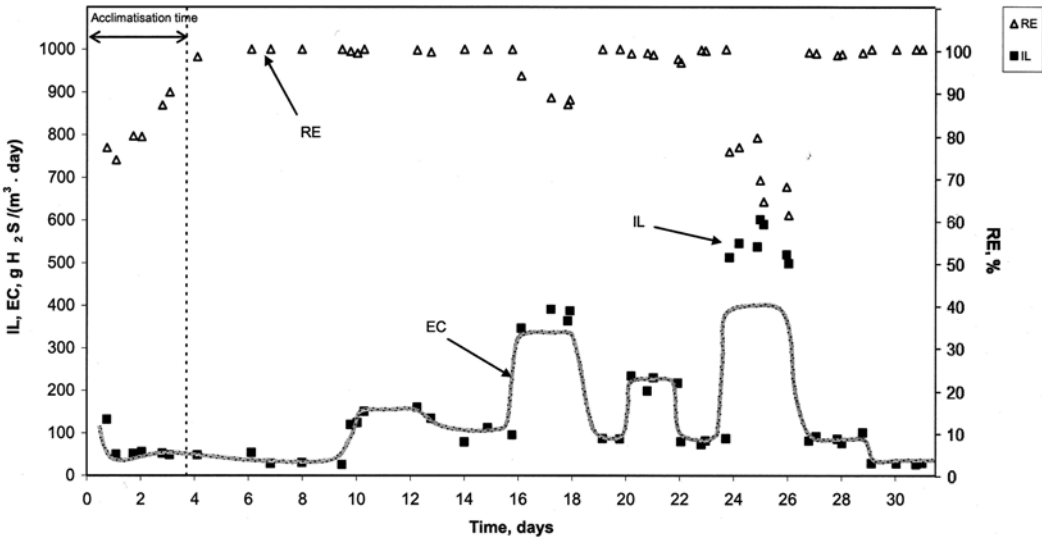

Fig 3. Variation of H_2S removal efficiency (RE), H_2S loading rate (IL), and biofilter elimination capacity (EC) as a function of time.

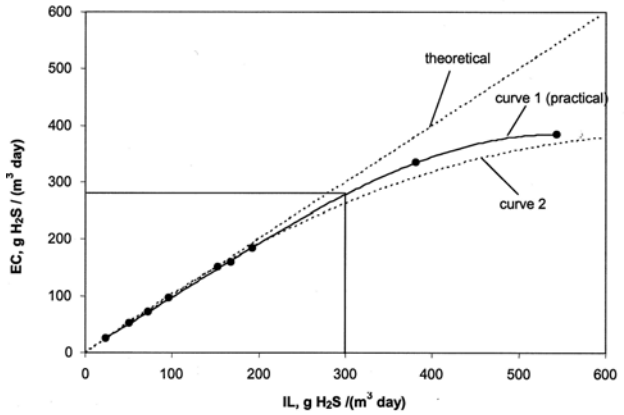

Fig. 4. Variation of biofilter elimination capacity (EC) versus H_2S loading rate (IL). Curve 1: Biotrickling filter packed with plastic fibres and volcanic rocks, 0.014-m^3 packing volume; Curve 2: Biotrickling filter packed with plastic fibres, 0.012-m^3 packing volume (Soreanu et al. 2007).

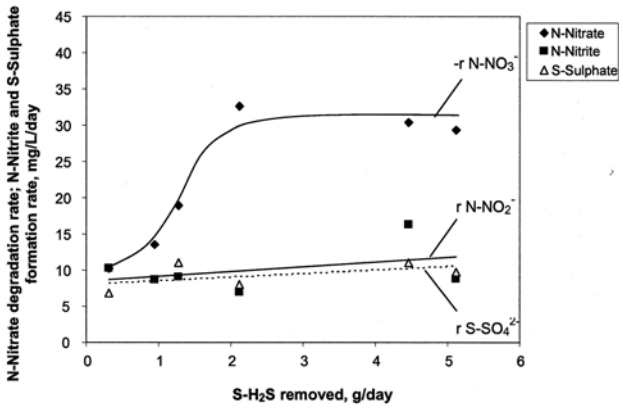

Fig. 5. Variation of N-nitrate degradation rate, and N-nitrite and S-sulphate formation rates as a function amount of daily hydrogen sulphide removed.

The variation of EC as a function of IL is plotted in Fig. 4 (curve 1). For comparison, this graph also includes the representation of the results obtained in a previous experiment carried out under similar experimental conditions (curve 2). Only the type of packing media was somewhat different in these studies (plastic fibres in Soreanu et al. 2007 versus plastic fibres plus volcanic rocks in the present study). The straight line corresponds to the maximum theoretical H_2S removal efficiency (RE = 100% and IL = EC). Good correspondence between IL and EC was obtained for a small IL range [up to 300 g of $H_2S/(m^3bed{\cdot}day)$], while for the highest IL range, EC tended to stabilize around 350 to 400 g of $H_2S/(m^3bed{\cdot}day)$ (curve 1). Therefore, it can be suggested that, under the current process operating conditions, the maximum elimination capacity corresponding to the maximum H_2S removal efficiency is approximately 300 g of $H_2S/(m^3bed{\cdot}day)$. These results are also in agreement with the previous reported results (Soreanu et al. 2007).

Degradation Pathway

A previous macrokinetic study was undertaken in order to determine the H_2S degradation pathway under constant H_2S input and nitrate-limiting and-nonlimiting conditions (Soreanu et al. 2008). In the present study, the experiment was carried out under varied IL input and nitrate nonlimiting conditions (nitrate in excess with respect to the nitrate requirement). The excess of nitrate as was used in this study does not affect the H_2S removal and assures a maximum potential of biodegradation over the entire period of the process (Soreanu et al. 2007, 2008). The formation of the corresponding degradation products was monitored as an indicator of hydrogen sulphide oxidation and the denitrification pathway.

The experimental variation of the nitrate degradation rate ($-r_{N\text{-}NO3}$, mg of N-nitrate consumed/L/day), nitrite formation rate ($r_{N\text{-}NO2}$, mg of N-nitrite formed/L/day) and sulphate formation rate ($r_{S\text{-}SO4}$, mg of S-sulphate formed/L/day) versus EC' (S-H_2S removed/day) are presented in Fig. 5. As can be observed, the nitrate degradation rate increased with EC' from 10.31 mg/L/day to a maximum of 32.57 mg/L/day, after which it remained constant at approximately 30 mg/L/day. Nitrite and sulphate formation rates fluctuated at approximately 12 ± 4 mg/L/day and 9 ± 2 mg/L/day respectively, in the range of EC' tested, thus suggesting that nitrogen and elemental sulphur are preferentially produced when the IL(EC) is increased.

Degradation and formation rates, as determined previously by Soreanu et al. (2008) for a loading of 1.5 g of H_2S per day were: $-r_{N\text{-}NO3}$ = 20.53 mg of $N\text{-}NO_3^-$/L/day; $r_{N\text{-}NO2}$ = 6.41 mg of $N\text{-}NO_2^-$/L/day; $-r_{SO4}$ = 9.09. These rates are in agreement with the results obtained in this study for a similar loading (i.e., for 1.35 g of H_2S per day, these rates are: $-r_{N\text{-}NO3}$ = 18.99 mg of $N\text{-}NO_3^-$/L/day; $r_{N\text{-}NO2}$ = 9.02 mg of $N\text{-}NO_2^-$/L/day; $-r_{SO4}$ = 11.08). Overall, it appears that the increase of H_2S loading rate occurs with the increase of S^0/SO_4^{2-} and N_2/NO_2^-, thus it dictates the ratio of degradation products in the system. The observed, moderately constant nitrate degradation and nitrite formation rates for IL' > 2.24 g of S-H_2S feed per day [168 g of H_2S feed/$(m^3bed{\cdot}day)$] or EC' > 2.11 g of S-H_2S removed per day (Fig. 5), suggest that the ratio N_2/NO_2^- is not significantly influenced by changes in S-input in the IL' tested range of 2.24 to 7.24 g of S-H_2S feed per day corresponding to an EC' between 2.11 to 5.12 g of S-H_2S removed per day.

Figures 6 and 7 present the ratio of S and N degradation products versus IL, as obtained from the corresponding mass balance.

According to Fig. 6, the amount of sulphate decreases from 50.46% down to 8.87% with an increase of IL from 24.04 to 168.32 g of $H_2S/(m^3bed{\cdot}day)$, and further decreases to trace levels at higher IL. This behaviour suggests that sulphate may be the major S-degradation

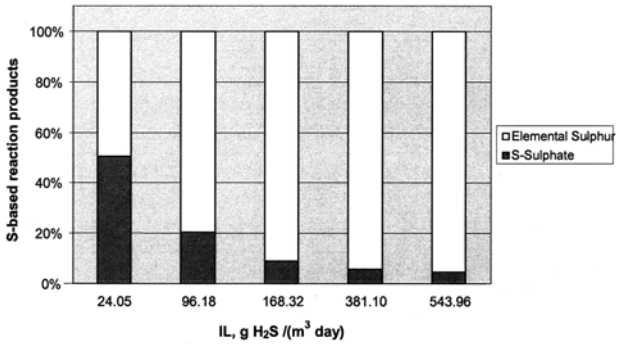

Fig. 6. The variation of the ratio of S-degradation products as a function of H_2S loading rate.

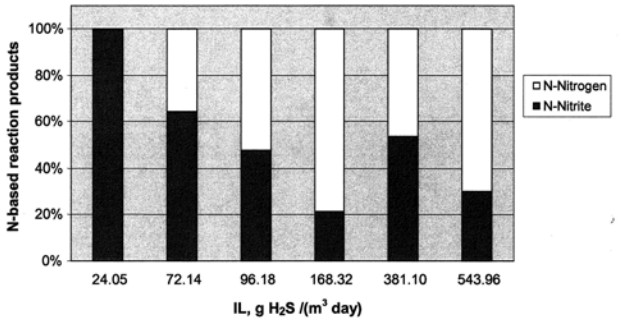

Fig. 7. The variation of the ratio of N-degradation products as a function of H_2S loading rate.

product at low IL [i.e., <24.04 g of H_2S/(m^3bed·day)] and elemental sulphur becomes the major S-degradation product at higher IL [i.e. >96.18 g of H_2S/(m^3bed·day)]. For example, for an IL of 96.18 g of H_2S/(m^3bed·day) (or 1.36 g of H_2S feed per day and, respectively, 1.27 g of S-H_2S removed per day), H_2S degradation occurs with the formation of 20.40% S-SO_4^{2-} and 79.59% S as S^0. The formation of elemental sulphur as the major degradation product seems to be related to a high IL, as has been reported by other authors (Buisman et al. 1990; Chung et al. 1996; Gevertz et al. 2000; McComas and Sublette 2001; Soreanu et al. 2007) either under aerobic or anoxic conditions. For example, under anoxic conditions and at a loading of 1.5 g of H_2S per day, Soreanu et al. (2008) reported the formation of approximately 15.25% S-sulphate and 84.75% elemental sulphur, which is in agreement with the above-mentioned results for similar loadings.

According to Fig. 7, the amount of nitrite produced decreases from 99.9 to 21.46% when the IL increases from 24.04 to 168.32 g of H_2S/(m^3bed·day), and fluctuates between 53.46 and 29.89% at higher IL. This observation suggests that at low available H_2S, nitrate is preferentially used in the nitrate-nitrite competition for the substrate (H_2S) (Tiedje 1988). Otherwise, at higher IL [i.e., > 96.18 g of H_2S/(m^3bed·day)], both nitrate and the reduced nitrite are consumed with the formation of nitrogen, usually as the main degradation product. Hence, the nitrate degradation pathway was dependent on the H_2S loads tested in this study, especially at smaller loading rates. Nitrate degradation during IL = 96.18 g of H_2S/(m^3bed·day) (or 1.35 g of H_2S per day) occurs with the formation of 47.50% N-nitrite and 52.50% N as N_2; that is comparable to results obtained by Soreanu et al. (2008) for a similar H_2S charge (1.5 g of H_2S per day) (i.e., 31.22% N-nitrite and 68.78% N as N_2). Gevertz et al. (2000) observed nitrate reduction at different sulphide (S^{2-}) concentrations using two novel chemolitotrophic nitrate-reducing, sulphide-oxidizing bacterial strains that were isolated from oil field brine and identified as *Thiomicroscpira denitrificans* (CVO) and genus *Arcobacter* (FWKO B). For CVO, a similar behaviour was obtained where the nitrite was observed to be the dominant N-degradation product (>60%) at low S^{2-} concentrations, compared with <50% at higher S^{2-} concentrations (2 and 3 mM, or 64 and 96 mg of S^{2-} per L). For FWKO B, nitrate reduction occurred with only nitrite as a degradation product, independent of S^{2-} concentration.

Interestingly, the stabilization of sulphate and nitrite formation is observed at the same IL [≥168.32 g of H_2S/(m^3bed·day)] (Fig. 6 and 7), suggesting that a different degradation pathway at high H_2S loading rates is followed (i.e., with the formation of mainly elemental sulphur and nitrogen). This observation is in agreement with McComas and Sublette (2001) who report that elemental sulphur becomes the major product of H_2S degradation involving *Thiobacillus denitrificans* when the H_2S loading rates exceed the maximum oxidation rate (i.e. when RE begins to decrease). Indeed, the change in the ratio of the degradation products is the result of the change of the degradation mechanism due to the change in the biological activity of the microorganisms with the load of the substrate in the system.

It appears that under non nitrate-limiting conditions, the degradation pathway of hydrogen sulphide was independent of the nitrate degradation pathway. Similarly, Soreanu et al. (2008) observed that the hydrogen sulphide degradation pathway at constant S input was not significantly influenced by the change in the N to S ratio resulting from changes in N input under non nitrate-limiting conditions. This behaviour is possible, taking into consideration that if one of the compounds (i.e., nitrate) is in excess, then the ratio of the degradation products (S^0/SO_4^{2-}, and, respectively, N_2/NO_2^-) depends on the initial concentration of the limited reactant, i.e., H_2S.

The modelling of the dual biological process for both sulphide and nitrate under limiting and nonlimiting conditions would be beneficial in order to predict the degradation pathway as a function of S or N changes occurring in the system.

Therefore, the reaction schemes (equations 1 to 10) shown in Table 1 can be drawn in order to describe the sulphur and nitrogen balance observed and thus the degradation pathway as a function of IL (note: trace

constituents have not been considered). Moreover, the linear variation of sulphate and nitrite percentages observed for IL ranging between 24.05 and 168.32 g of H_2S/(m^3bed·day) allows the prediction of the degradation product ratio as a function of IL from the corresponding linear regressions: (Percentage Compound, %) = *f*(IL·RE) (equations 11 to 14).

TABLE 1. Sulphur and nitrogen balances describing the degradation pathway

IL [a]	*Reaction scheme* [b]	*Equation No.*
24.05	$S\text{-}H_2S \rightarrow 0.51\ S\text{-}SO_4^{2-} + 0.49\ S^0$	(1)
	$N\text{-}NO_3^- \rightarrow N\text{-}NO_2^-$	(2)
96.18	$S\text{-}H_2S \rightarrow 0.20\ S\text{-}SO_4^{2-} + 0.80\ S^0$	(3)
	$N\text{-}NO_3^- \rightarrow 0.47\ N\text{-}NO_2^- + 0.53\ N\text{-}N_2$	(4)
168.32	$S\text{-}H_2S \rightarrow 0.09\ S\text{-}SO_4^{2-} + 0.91\ S^0$	(5)
	$N\text{-}NO_3^- \rightarrow 0.22\ N\text{-}NO_2^- + 0.78\ N\text{-}N_2$	(6)
381.10	$S\text{-}H_2S \rightarrow S^0$	(7)
	$N\text{-}NO_3^- \rightarrow 0.54\ N\text{-}NO_2^- + 0.46\ N\text{-}N_2$	(8)
543.96	$S\text{-}H_2S \rightarrow S^0$	(9)
	$N\text{-}NO_3^- \rightarrow 0.29\ N\text{-}NO_2^- + 0.71\ N\text{-}N_2$	(10)

[a] IL units, g of H_2S/(m^3bed·day)
[b] Subject to experimental variation

$$S^0,\ \% = 0.311x + 44.512 \quad (11)$$
$$N \text{ as } N_2,\ \% = 0.5774x - 8.8574 \quad (12)$$
$$N\text{-Nitrite},\ \% = -0.5774x + 108.86 \quad (13)$$
$$S\text{-Sulphate},\ \% = -0.311x + 55.488 \quad (14)$$

Where x = IL [g of H_2S/(m^3bed·day)]·RE (%); these equations are suitable for IL = 24.04 to 168.32 g H_2S/(m^3bed·day).

Nitrate Demand

Figure 8 shows the variation of nitrate demand (g of $N\text{-}NO_3^-$ per g of H_2S removed) versus the amount of hydrogen sulphide removed per day (EC', g of H_2S removed per day). The process is characterized by chemical and biological composites that change as a result of reaction conditions. Experimentally, it was observed that nitrate demand (g of $N\text{-}NO_3^-$ consumed per g of H_2S degraded) decreases from 0.71 to 0.12 g of $N\text{-}NO_3^-$ per g of H_2S removed with an increase in the amount of H_2S degraded from 0.34 to 5.42 g of H_2S removed per day. This behaviour may be possible with regard to the experimentally determined degradation pathways presented in Table 1, and to the theoretical reactions and their corresponding theoretical nitrate demands previously presented in Soreanu et al. (2008). The degradation pathways presented in Table 1 were determined from the sulphur and nitrogen balances. As can be seen, at small H_2S loading rates [IL = 24.05 g of H_2S/(m^3bed·day)] used in this study, H_2S degradation occurred with the formation of both sulphate and elemental sulphur, while nitrate degradation occurred mainly with the formation of nitrite. These reactions agree with the theoretical reactions (7) and (8) from Soreanu et al. (2008), corresponding to the highest theoretical nitrate demand (i.e., average of 1.02 g of $N\text{-}NO_3^-$ consumed per g of H_2S degraded), as also observed in this study (i.e., 0.71 g of $N\text{-}NO_3^-$ consumed per g of H_2S degraded). The smallest nitrate demand (i.e., 0.13 to 0.15 g of $N\text{-}NO_3^-$ consumed per g of H_2S degraded) recorded in this study was observed at a high H_2S loading rate [i.e., IL ≥ 168.32 g of H_2S/(m^3bed·day)] when hydrogen sulphide was degraded to mainly elemental sulphur, while nitrate degradation occurred with the formation of predominantly nitrogen, and the balance was nitrite. Indeed, according to Soreanu et al. (2008), the smallest theoretical nitrate demand (i.e., 0.16 g of $N\text{-}NO_3^-$ consumed per g of H_2S degraded) may occur when elemental sulphur and nitrogen are the main degradation products. At the medium H_2S loading rates [i.e., 96.18 g of H_2S feed/(m^3bed·day) or 1.36 g of H_2S feed per day] used in this study, elemental sulphur and sulphate were the major and minor products of biodegradation, respectively, while nitrite and nitrogen were also present in the system as a result of nitrate degradation. Nitrate demand recorded under such conditions was 0.33 g of $N\text{-}NO_3^-$ consumed per g of H_2S degraded. A similar ratio of degradation products and nitrate demand was experimentally and theoretically obtained by Soreanu et al. (2008) for a similar H_2S loading rate. As can be seen in Fig. 8, the nitrate demand remained constant at 0.33 ± 0.01 g of $N\text{-}NO_3^-$ consumed per g of H_2S degraded for EC' between 1.01 and 2.24 g of H_2S removed per day.

Operation with Two Bioreactors in Series

In practice, a prefilter may be used in order to reduce the loading of pollutants to the second filter and thus increase the overall performance of the biofiltration system. This dual bioreactor design was thus undertaken using two bioreactors in series (i.e., 0.012 and 0.014 m^3, respectively). As can be seen in Fig. 9, the RE increased from 35.14% after one reactor [when 793.33 g of H_2S/(m^3bed·day) was fed in the 0.012 m^3 reactor] to a

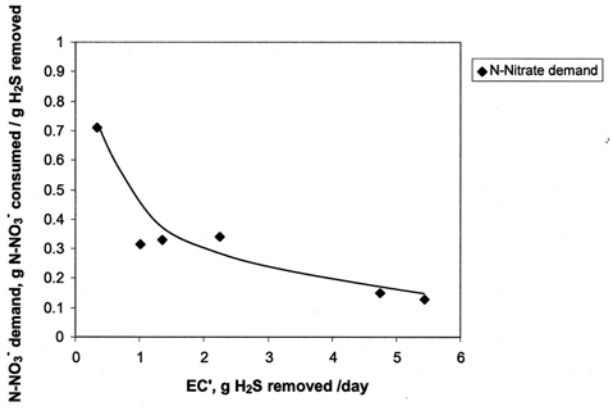

Fig. 8. Variation of nitrate demand as a function of biofilter elimination capacity.

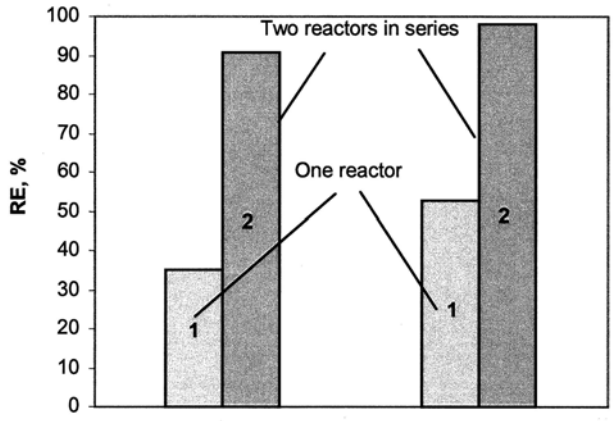

Fig. 9. Increasing H_2S removal efficiency by operating two reactors in series. Reactor(I): Biotrickling filter packed with plastic fibres (0.012-m^3bed volume, Soreanu et al. 2007); Reactor(II): Biotrickling filter packed with rocks and plastic fibres (0.014-m^3bed volume).

cumulative RE of 90.6% after two reactors in series. In another experimental trail, the RE increased from 52.73% [when 537 g of H_2S/(m^3bed·day) was fed in the 0.012 m^3 reactor) to a cumulative RE of 98.02% after two reactors in series. These results suggest that under the above-mentioned conditions, the RE can be improved up to 2.5 times with the addition of a second reactor. As expected, the addition of the second reactor decreased the overall IL by increasing the total packing volume to 0.026 m^3, which resulted in an EC quite close to the EC observed when a similar IL was loaded in one reactor (0.014-m^3 bed volume). These results indicate that the packing media volume and/or the type of packing material is another significant factor to be considered for the improvement of the process performance, especially for higher H_2S loading rate applications.

Regeneration and Sulphur Recovery from Packing Media

One of the major problems reported for biofilters is the excessive production of the biomass leading to the fouling of packing media and the increase of the pressure drop across the biofilter (Devinny et al. 1999). These problems were not observed in present and previous similar studies, likely due to the anoxic characteristic of the process (Soreanu et al. 2008). Elemental sulphur production, although visually observed as a very fine light yellow powder, does not interfere with the operation of the biofilter (i.e., clogging), probably due to its hydrophilic nature (Seidel et al. 2006). A very simple maintenance procedure to remove excess sulphur is recommended, and involves the occasional flushing of the column with nutrient solution (i.e., monthly, depending on process). This procedure was carried out in order to avoid excess accumulation of elemental sulphur in the packing media.

TABLE 2. Analysis of the solid collected from the packing bed (fibre)

Parameter	*% (per solid)*
Sulphur (extractable)	83.25
Sulphate	1.04
Thiosulphate	ND
Iron (extractable)	0.628
Sodium (extractable)	2.59
Ammonia as N	ND
Nitrite as N	0.27
Nitrate as N	1.06
Other impurities [b] / losses	11.16

[a] ND = not detected.
[b] Other impurities; particles of biomass, fibres, etc.

This procedure was also successfully applied in previous studies, without any negative effect on the operational and process performance of the biofilter. The recovery of sulphur from the "washing" solution is possible, if desired. Sulphur recovery was not a main purpose of this study, but it is interesting to note that recovery of the sulphur deposited on the fibres was also possible by drying and shaking the plastic fibre media. Table 2 presents a summary characterization of the sulphur recovered from the plastic fibres. High sulphur purity was obtained (83.25% sulphur), thus offering new technology perspectives.

Conclusion

This paper presents a study on the performance of an anoxic biotrickling filter treating H_2S in biogas. The experiments were carried out at several loading rates ranging between IL = 20 to 550 g of H_2S/(m^3bed·day) under nitrate-nonlimiting conditions. The maximum elimination capacity corresponding to the maximum H_2S removal efficiency (>95%) was found to be approximately 300 g of H_2S/(m^3bed·day). An increase of the IL to a level more than this value resulted in a decrease of RE. The operation of two bioreactors in series demonstrated a significant improvement in process performance. The H_2S degradation pathway was also found to be influenced by the change in IL. At small to medium IL [i.e., 24.05 to 96.18 g of H_2S/(m^3bed·day)], the H_2S degradation occurs with the formation of both sulphate and elemental sulphur, while at higher IL [IL ≥ 168.32 g of H_2S/(m^3bed·day)], elemental sulphur is the major degradation product. It also appears that under non nitrate-limiting conditions, the degradation pathways of the hydrogen sulphide were independent of the nitrate degradation pathway, while the nitrate degradation pathway was dependent on the H_2S loading rate, when, for example, nitrogen formation was favoured at high H_2S loading rates [IL ≥ 168.32 g of H_2S/(m^3bed·day)]. The technology presented requires simple maintenance of the biotrickling filter, and sulphur recovery is also possible.

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