Biological treatment of hydrogen sulphide from landfill site biogas

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Abstract

Hydrogen sulphide (H_2S), a highly corrosive gas, is found in biogas due to the biodegradation of proteins and other sulphur containing compounds present in feed stock during anaerobic digestion. The presence of H_2S is one of the biggest factors limiting the valorisation of biogas. It should be removed prior to application of biogas in an electric generator or industrial boiler. In this study, a laboratory scale bioreactor of 1 L volume was operated for one month. The main objective of that is to determine the impact of the operation condition for designing and operating a pilot-scale bio-trickling filter (BTF). The bio-trickling filter packed with stainless-steel pall rings and inoculated with H_2S oxidizing consortium has been designed to process 1 to 10 SCFM biogas and utilized to determine the removal efficiency of high strength hydrogen sulphide from a landfill sites biogas (LETs). The bio-trickling filter was operated for 3 months at Valoris landfill site, QC, Canada. The inlet gas was fed to the bottom of the bio-trickling filter, while the solution was sprayed from a nozzle at the top of the bio-trickling filter to maintains the bed moisture and provides the essential nutrients for the microbial activity. The Inlet H_2S concentrations varied between 900 to 1500 ppmv. Results indicate that the biofiltration system, containing stainless-steel pall rings as a filter material, removed H_2S with efficiencies ranged between 94% and 97% at hydraulic retention time (HRT) of 0.9 min.

1.Introduction

Recently, various attempts have been made to develop renewable and alternative energy sources to minimize global environmental problems and green house gas emissions. As one of the prominent renewable energy sources, biogas produced by anaerobic processes using industrial and domestic wastes has been emerged as a green energy source as well as an alternative to reduce greenhouse gas emissions. At many landfill sites (LETs), biogas is being collected and used to generate heat and electrical energy. As a result, the effective use of biogas not only supplies a sustainable energy source but also minimize a release of methane, which is the main component of biogas and its green house effect is approximately 21 times higher than carbon dioxide (Lee et al., 2003).

However, biogas produced from LETs commonly contains impurities such as hydrogen sulphide (H_2S). H_2S can be generated from a variety of sources, and it is a very strong malodorous compound detected even at a low concentration lower than 0.1 ppm. Many investigations have reported that a concentration range of hydrogen sulphide from biogas LETs was found to be up to 5000 ppmv. The impurity of biogas, therefore, needs to be pre-treated to avoid facility corrosion, unnecessary production of by-products, and possible public exposure and complaints (Lee et al., 2007; Taliwa et al., 2009).

In order to reduce the emissions of this contaminant, various physical, chemical and biological alternatives have been developed. Among these, biofiltration of H_2S is a technological avenue with high potential and low operating costs. In the biofiltration processes, hydrogen sulphide in the gas phase is first dissolved into microbial media containing sulphur oxidizing bacteria, and the bacteria subsequently oxidize hydrogen sulphide in the presence of oxygen in the liquid phase (Duan et al., 2006; Park et al., 1999). These robust systems are effective in removing low concentrations of H_2S for residence times of less than one minute and initial concentrations corresponding to those encountered in biogas generated by landfills (1000-2000 ppmv). To do this, a bacterial consortium has been adapted, from activated sludge, to oxidize H_2S to sulphate while using, as a carbon source, the CO_2 contained in the biogas.

In a first phase of this study, a laboratory bioreactor of 1 litter was operated for one month. The influence of the operating conditions was determined (pH, frequency of purges and nutrient additions, etc.). Taking into account the impact of the operation conditions determined at the laboratory scale, the design, construction and operation of a pilot-scale bioreactor dedicated to the treatment of a biogas from LETs at Valoris landfill site, QC, Canada was proceeded. This bioreactor consists of two-phase bio-trickling filters. The bioreactor has been designed to process 1 to 10 SCFM biogases and utilized to determine the removal efficiency of hydrogen sulphide from raw biogas.

2. Materials and methods

2.1 Preparation of bacteria consortium

An aerobic activated sludge used in this study was obtained from the Magog Wastewater Treatment Plant (Qc, Canada) with a suspended material concentration of 3.5 g/L. The later has been used in order to acclimatize a H_2S oxidizing consortia. Acclimatization was carried out using a H_2S oxidizing consortia which are chemolithotroph bacteria known for their ability to grow in sulphur-containing media (Schedel et al., 1975). During The acclimation, the nutrient solution (culture medium) was used for maintaining microorganisms and applied as the medium for the immobilization process and recirculated liquid during the bioreactor operation. The culture medium contained the following 15 g/L $Na_2S_2O_3.5H_2O$, 4g/L K_2HPO_4, 4 g/L KH_2PO_4, 0.8 g/L $MgSO_4.H_2O$, 0.4 g/L NH_4CL, 22 g/L $NaHCO_3$, 22 g/L $ZnSO_4.7H_2O$, 5.54 g/L $CaCl_2$, 5.06 g/L $MnCl_2.4H_2O$, 4.99 g/L $FeSO_4.7H_2O$, 1.1 $(NH_4)6MO_7O_{24}.H_2O$, 1.57 $CuSO_4.5H_2O$, 1.61 g/L $CoCl_2.6H_2O$ and 2 g/L yeast extract. The final pH of this medium was adjusted to 7 by using 1 N NaOH or HCl solution.

2.2 Laboratory scale bioreactor

A laboratory scale bioreactor was constructed and used for the removal of hydrogen sulphide. The bioreactor used in this study is shown in Figure.1. The latter was made of glass with total volume of 1000 mL. The bioreactor was inoculated for three days by bacterial suspension with an optical density equivalent to 4.5 (absorbance at 600 nm). After this acclimation period, the culture media was added to the reactor to improve the bacterial growth. The reactor was continuously supplied with a synthetic gas whose composition is H_2S (0.07 to 0.2% v/v), CO_2 (20% v/v) and air (100% balance) for one month. The parameters used for these laboratory tests are summarized in Table 1. During the lab scale tests, the initial H_2S concentration was initially 730 ppmv, then it was gradually increased to 1000 and 2000 ppmv at 3-day intervals. The gradual supply of hydrogen sulphide is intended to acclimate the bacterial consortium to the new conditions and resources available. The change of one part (300 ml) of culture medium took place, on average, every 72 hours. This renewal of the culture medium was done when there was a decrease in the growth rate of the biomass (optical density) in the reactor. During the tests, and in order to avoid clogging of the bubbler used, a daily check was made by opening the reactor and cleaning the bubbler with compressed air.

Table 1. The parameters of the laboratory test.

Parameters	**Value**
Volume (L)	1
Flow rate (L/min)	0.5 – 1
Retention time	1 - 2 min
Reactor pressure (atm)	Atmosphere
Gas pressure before injection in the reactor (atm)	1.7
Concentration of H_2S (ppmv)	730 – 2000
Concentration of CO_2 (%v/v)	20
Air humidify	Balance 100 %

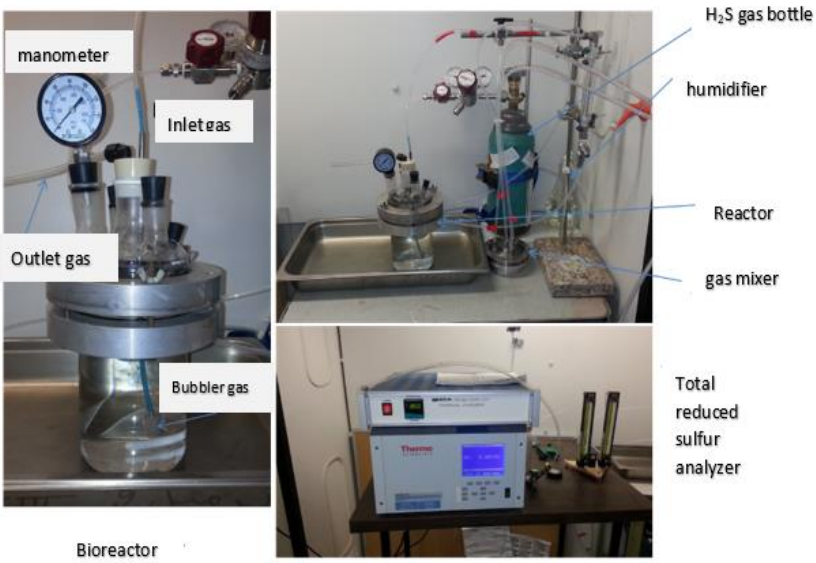

Figure 1: A laboratory scale bioreactor (Diameter of the bioreactor = 10 cm & Height of the bioreactor = 17 cm)

2.3 Pilot scale bio-trickling filter

The experiments were performed using two pilot-scale bio-trickling filters in series and made of PVC as shown in Figure.2. The first bio-trickling filter (BFT 1) has an inner diameter of 12.5 cm and a height of 40 cm. While, the second bio-trickling filter has an inner diameter of 11.5 cm and a height of 20 cm. The two bio-trickling filters packed with same packing material (stainless-steel pall rings) with diameter of 16 mm, as shown in Figure 3. The LETs biogas consisted of 52% v/v of methane, 39% v/v of CO_2, 11% v/v of CO, 1.2 % of O_2, and 1000-2000 ppmv of H_2S. The flow rates and inlet concentrations were controlled via flow meter and regulators on the pipes for biogas. The air flow in BTF1 was constant to be 4% v/v of O_2 during the operation period. The inlet gas was fed to the bottom of the BTF 1 and BTF 2 at a constant flow rate of 2.3 L/min and 1.2 L/min, respectively. Part of the pre-treated biogas was exhausted after BTF1. The system was operated at Valoris landfill site, QC, Canada. Throughout the experimental period, the inlet and outlet H_2S concentrations were measured periodically, and the percolate in the bottom of each bio-trickling filter was evaluated to determine its pH and sulphate concentration. In this experiment, the bio-trickling filter was first inoculated with activated sludge bacteria for 20 d. The medium prepared for the cultivation of the bacteria contained the followings 5 g /L $Na_2S_2O_2.5H_2O$, 1.5 g/L KH_2PO_4, 1.5 g /L K_2HPO_4, 0.4 g/L NH_4Cl, 0.2 g/L $MgCl_2.6H_2O$, and 3.1 g/L glucose and it was added into the reservoir 1. This irrigation maintains the bed moisture and provides the essential nutrients for the microbial activity, as well as the removal of the by-products produced during the biological reaction. The flow rate of the irrigation solution was constant 2 m^3/h at intervals of 60 min, discharged from the bottom, and recycled. The operational conditions of BTF 1 and BTF 2 are summarized in table 2.

Table 2. The operational conditions of BTF 1 and BTF 2.

Parameters	BTF 1	BTF 2
Dimensions	12.5 cm × 40 cm	11.5 cm × 20 cm
Effective volume (L)	110	25
Flow rate (L/min)	2.3	1.2
Hydraulic Retention time @1scfm	3.9 min	0.9 min
pH	2	7
Concentration of inlet H_2S (ppmv)	900	100
Air humidify	4%	--

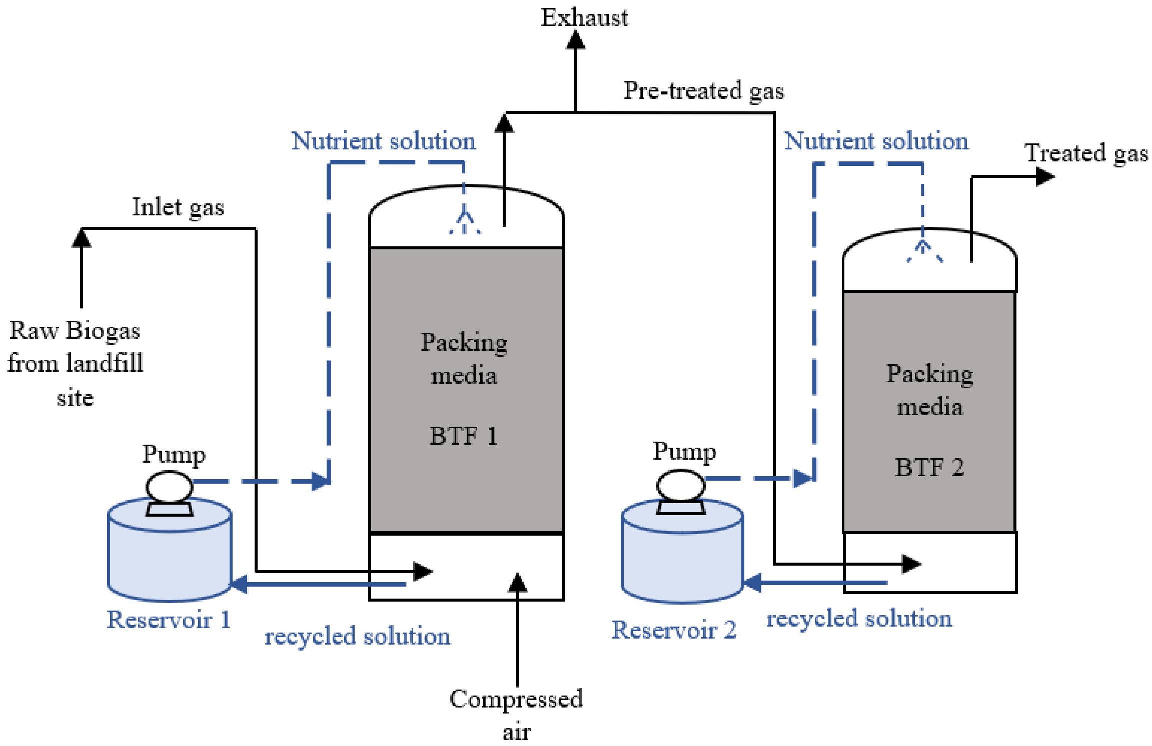

Figure 2: Pilot-scale bio-trickling filter in Valoris site landfill

Figure 3: Stainless-steel pall rings

2.4 Analytical models

Inlet and outlet H_2S gas concentrations were continuously measured by using a Colorimetric gas detection tubes (Gastec corporation, Higashi-ku, Fukuoka-Shi, JAPAN). The detection ranges of the H_2S gas tubes were 1–2000 and 1–200 ppm for inlet and outlet H_2S gas concentrations, respectively. The concentration of sulphate ions was measured by using a spectrophotometric method (Hach, Sulphate). The growth of the microorganisms was monitored by measuring optical density of the medium growth at 600 nm (Hach DR-2000 spectrophotometer, 25 ml cuvette). The removal efficiency of H_2S was calculated using the following equation:

$$RE = \frac{C_{in} - C_{out}}{C_{in}} \times 100$$

where, RE: removal efficiency (%); C_{in}: inlet H_2S concentration (ppm);C_{out}: outlet H_2S concentration (ppm). The pH of the nutrition solution was measured using a digital calibrated pH-metre (Mettler Toledo AG). The COD was measured according to the Standard Methods for the Examination of Water and Wastewater (1995) at the laboratory of environmental engineering at University of Sherbrooke. The CIP-MS methodology was used for heavy metals quantification in wastewater.

3. Results and discussion

3.1 Biodegradation test of H_2S in the laboratory

The acclimation of the bacterial consortium was performed on a medium for allowing the enrichment of the H_2S oxidizing bacteria consortia. Figure 4 shows that the optical density increased after 2 operation days. On the other hand, the high production of sulphate ions was proportional with the increase of the biomass. It was noted that the acclimation was carried out in a mineral autotrophic medium with sodium bicarbonates, sodium thiosulphates and yeast extract as a carbon source, in order to maintain the CH_4 content of the biogas.

The tests started using a low concentration of H_2S (730 ppmv) in the gaseous stream. The culture medium was renewed each time there is a decrease in biomass (observed via a decrease in optical density) as well as the concentration of sulphate ions. 30% of volume was exchanged by a new nutritional solution. The results of the first tests (first week of testing) are presented in Figures 5, 6 and 7. The results indicate that the H_2S removal capacity was around 99% for an initial concentration of 2400 ppmv on average, corresponding to H_2S load of 330 g $S/m^3/h$. Similarly, sulphate ion production and bacterial growth correlated with the progress of H_2S removal.

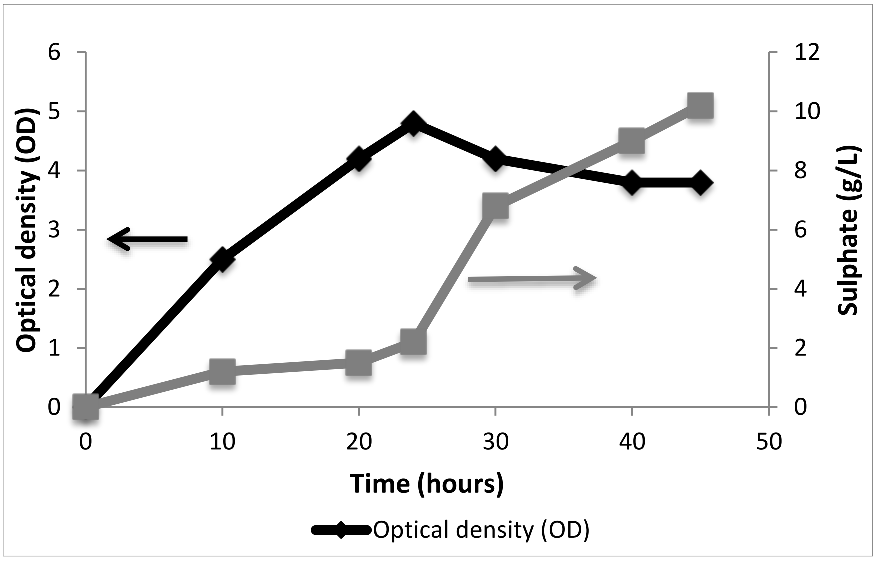

Figure 4: Evolution of biomass and sulphate ions concentrations during acclimation tests (T = 25 ° C, 60 rpm).

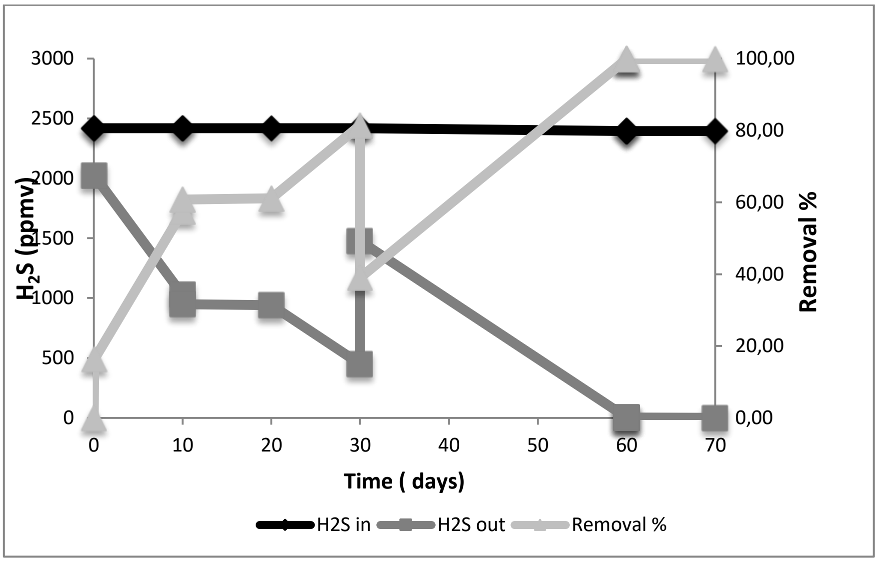

Figure 5: Monitoring the H_2S concentration at the inlet and the outlet of the bioreactor and the rate of elimination. (T = 25 °C, 60 rpm, Initial biomass: OD600 = 3.75)

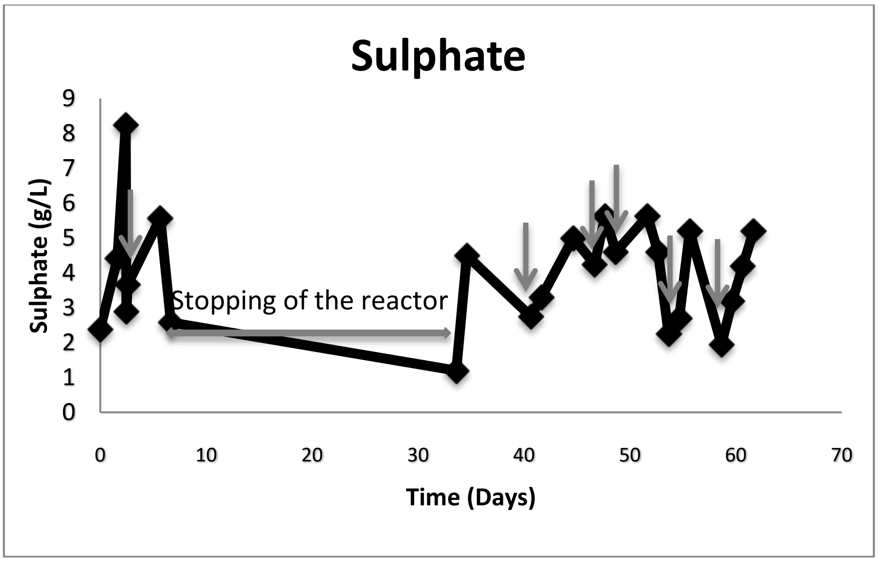

Figure 6: Evolution of the concentration of sulphate ions (T = 25 ° C, 60 rpm, Initial biomass: OD600 = 3.75). The arrows in grey correspond to the times when the culture medium was renewed

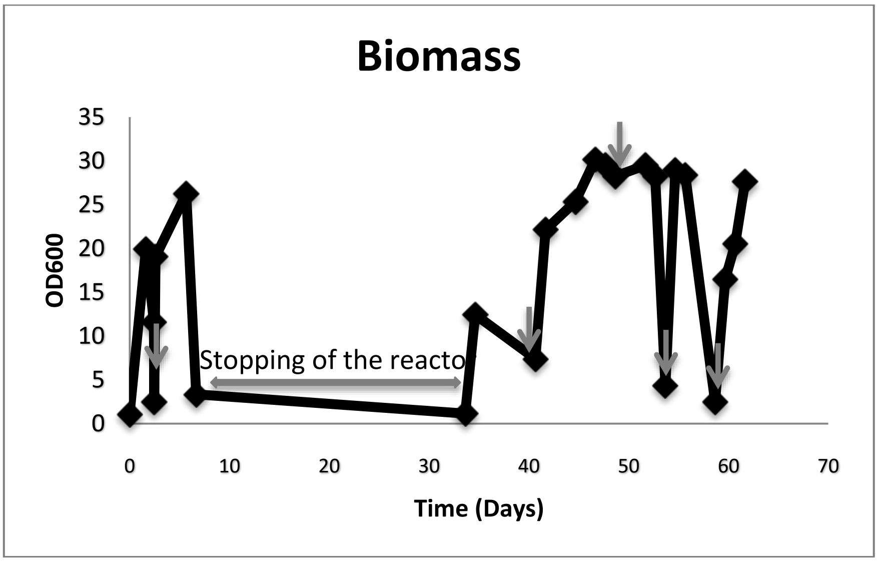

Figure 7: Evolution of the biomass concentration (T = 25 ° C, 60 rpm, Initial biomass: OD600 = 3.75). The arrows in grey correspond to the times when the culture medium was renewed.

3.2 The performance of the pilot scale biofiltration treatment system on landfill site

The feasibility of using a bio-trickling filters system to treat hydrogen sulphide from the real biogas in landfill site was investigated in this study. The inlet H_2S concentrations were varied from 900 to 1220 ppmv. Sampling and analyses were conducted continuously over a 3-month period (from July 2017 to October 2017). The H_2S concentration was periodically determined in the inlet and outlet of the bio-trickling filter, then removal efficiency was calculated. In BTF 1, the pH of the recirculation nutrient solution decreased to 2. Such low pH causes less solubility of H_2S in the liquid medium and hence some of the H_2S escapes without being treated. Therefore, the second bioreactor with a pH of 7 captures H_2S and then oxidizes it to sulphate. The average H_2S removal efficiencies of the biofiltration system after adding the second bio-trickling filter were above 97 % for the majority of the operation time. For inlet H_2S concentrations ranging from 900 to 1550 ppmv, higher removal efficiencies were still achieved at 97 % and approximately 50 ppm of H_2S gas was detected in the outlet as can be seen in Figure 8. Results indicate that the biofiltration system, containing stainless-steel pall rings as a filter material, removed H_2S with efficiencies ranged between 94% and 97 % for H_2S inlet concentrations at the range of 900 to 1500 ppmv H_2S.

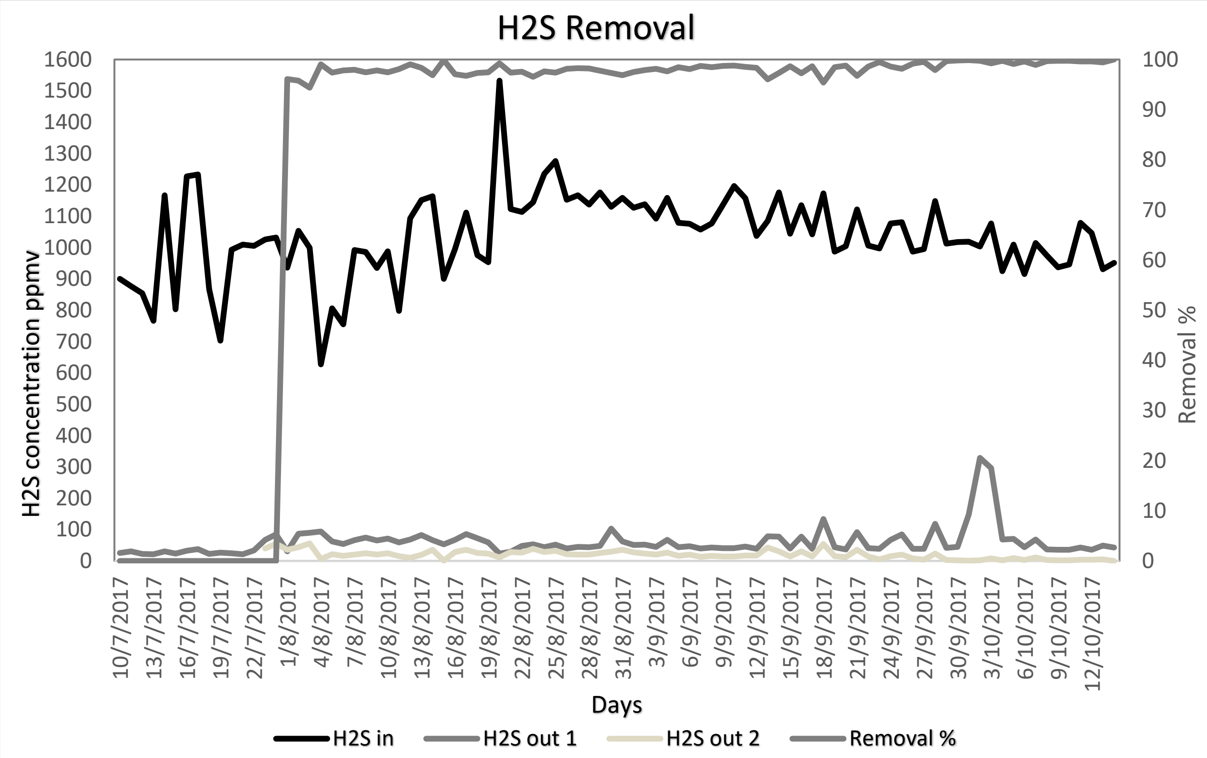

Figure 8: Performance of the bio-trickling filter bed for treating H_2S over an operational period of 90 days in landfill site.

3.3 Characterisation of liquid phase of bio-trickling filter treating H_2S

The liquid phase (nutrient solution) is an essential part in treating the biogas. The nutrient solution is used to provide the necessary nutrients for the microorganisms, to control the pH of the reaction media and to solubilize the H_2S so that it can be bio-transformed. In this study, the average characteristics of the produced liquid are based on the measurement of pH, COD and sulphate concentration of the percolate (Table 3). During the later period of the experiment, the pH of the medium was quite acid because of the accumulation of the large amount of sulphuric acid. The mixed wastewater from the discharges of bioreactors 1 and 2 had a pH of 5.

Based on the characteristics of the mixed wastewater produced from the biofiltration system, it was observed that the high concentration of chrome, iron and nickel were leached to the liquid. These contaminants came from the packing media used (consisting essentially of stainless steel) and not from the biogas treatment (Montebello et al., 2014).

The COD of the initial nutrition solution before recirculation was in the range of 20 mg/L. The COD of the liquid increased at the outlet of the bio-trickling filter, and it was 1520 mg/L, while the Valoris standards of wastewater allow only COD of 150 mg/L. Therefore, the produced liquid must be treated in order to be used in irrigation or filtration process.

Table 3. Averaged characteristics of the produced mixed wastewater.

Parameters	**Value**
pH	5
Chemical oxygen demand (COD)	1520 mg/L
Total suspended solid (TSS)	143 mg/L
Volatile suspended solid (VSS)	47 mg/L
Sulphate ion (SO_4^{2-})	22200 mg/L
Calcium (Ca)	42.9 mg/L
Chrome (Cr)	351 mg/L
Iron (Fe)	1500 mg/L
Potassium (K)	440 mg/L
Magnesium (Mg)	54.5 mg/L
Manganese (Mn)	22.9 mg/L
Nickel (Ni)	185 mg/L
Phosphorus (P)	440 mg/L

4. Conclusion

In this study, the two-phase bio-trickling filter was applied to treat high strength hydrogen sulphide stream from landfill site biogas. The key observations and conclusions that can be drawn from this study are given below:

- The biofiltration system, containing stainless-steel pall rings as a filter material, removed H_2S with efficiencies ranged between 94% and 97 % for H_2S inlet concentrations at the range of 900 to 1500 ppmv H_2S.
- Approximately 50 ppmv of H_2S gas was detected in the outlet.
- It was observed that the high concentration of chrome, iron and nickel were leached to the produced liquid. These contaminants came from the packing media used (consisting essentially of stainless steel) and not from the biogas treatment.

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