

ASSESSMENT OF HYDROGEN SULFIDE REMOVAL FROM BIOGAS USING A FIELD SCALE ANOXIC BIOTRICKLING FILTER

Pirolli, M¹; Da Silva, M.L.B.²; Mezzari, M. P.³; Michelon, W.¹; Prandini, J.M¹; Soares, H. M.¹

¹ Department of Chemical Engineering, Federal University of Santa Catarina, Florianópolis-SC, Brazil, (e-mail: *pirollimateus*@gmail.com; eng.williammichelon@gmail.com; jeanprandini@hotmail.com soares@enq.ufsc.br).

² Embrapa Świne and Poultry, Concórdia, SC – Brazil, (e-mail: *marcio.busi@embrapa.br*).

³ Biotechnology and Sciences Program, West University of Santa Catarina – UNOESC, Videira, SC – Brazil (melissa.mezzari@unoesc.edu.br)

ASSESSMENT OF HYDROGEN SULFIDE REMOVAL FROM BIOGAS USING A FIELD SCALE ANOXIC BIOTRICKLING FILTER

Pirolli, M¹; Da Silva, M.L.B.²; Mezzari, M. P.³; Michelon, W.¹; Prandini, J.M¹; Soares, H. M.¹

¹ Department of Chemical Engineering, Federal University of Santa Catarina, Florianópolis-SC, Brazil, (e-mail: *pirollimateus*@gmail.com; eng.williammichelon@gmail.com; jeanprandini@hotmail.com soares@enq.ufsc.br).

² Embrapa Świne and Poultry, Concórdia, SC – Brazil, (e-mail: *marcio.busi@embrapa.br*).

³ Biotechnology and Sciences Program, West University of Santa Catarina – UNOESC, Videira, SC – Brazil (melissa.mezzari@unoesc.edu.br)

Abstract

Hydrogen sulphide is one of the most toxic and corrosive compound present in swine-derived biogas streams. In this study, a field scale biotrickling filter for the removal of hydrogen sulfide was investigated. A Biofilter packed with supporting biofilm materials was fed continuously with a proprietary nutrient solution and operated for over 73 days. The system has been operating with a H₂S inlet concentrations ranging from 1,000 to 3,000 ppm. Significant removal efficiencies >95% was demonstrated. pH of the stock feeding solution decreased from 6.2 to as low as 3.5 within couple days. The resulting drop in pH provided circumstantial evidence to support biological H₂S oxidation to sulphuric acid by sulfide-oxidizers. Sulfur precipitation was also observed to occur. The results suggested that H₂S removal from biogas stream can be efficiently achieved using portable, low cost and maintenance free biotrickling filters.

Keywords

Biogas; Biotrickling filter; Hydrogen sulfide; Desulfurization.

INTRODUCTION

The use of biogas as a potential source of renewable biofuel has been drawing attention in many countries. However, biogas often contains high concentrations (0.1-2%) of toxic hydrogen sulphide (H₂S) (Anet .2013) that must be removed from gas stream to prevent overall infrastructure corrosion and failures. Biogas purification methods can be classified into two main categories which involve physical-chemical or biological processes (Abatzoglou, 2009). Biological methods such as the use of biotrickling filters (BTFs) are technically effective and economically feasible compared to other traditional physical-chemical processes (Omri, 2013). Moreover, biological filtering processes are less prone to contribute to environment pollution (Elias et al., 2002; Kim et al., 2002; Oyarzún et al., 2003; Sercu et al., 2005). In these biological systems, a source of sulfide-rich gas stream typically passes through a packed-bed closed reactor containing suspended or fixed microorganisms that are able to oxidize H_2S into harmless byproducts (Ma et al., 2006). When degrading inorganic compounds such as hydrogen sulphide, autotrophic bacteria utilize carbon dioxide as a carbon source resulting in the production of new biomass and sulphate or elemental sulphur (Barona et al., 2004).

Although the use of biofilters have been extensively reported, its development and implementation still holds challenges when it comes to field scale functionality, maintenance of removal efficiencies over time and operating costs. For instance, process controls techniques such as the introduction of selected microorganisms and the metabolic maintenance of system's microbiology, oxygen injection and nutrient formulations are major factors affecting the economic feasibility of the process as well

as labor requirements. For that matter, the objective of this study was to evaluate the removal efficiency of a low cost and maintenance free field scale biotrickling filter to biological remove sulphide (H_2S) from biogas produced in anaerobic digester treating swine wastewater.

MATERIAL AND METHODS

Biotricking filter setup and operation

A 1.5m high 0.2 m diameter PVC was used to build the biotrickling filter (BTF). The reactor was packed with supporting materials for biofilm fixation and fed with a proprietary nutrient solution blend (patent pending). The gas stream passing through the system was adjusted initially to 400 mL/min using a rotameter (Omega) which resulted in a hydraulic retention time of 97 min. The reactor was continuously fed biogas from an upflow anaerobic sludge blanket reactor (UASB) located at EMBRAPA (Concórdia, SC, Brazil) wastewater treatment facility. Fig. 1 provides a schematic of the setup. Liquid samples were collected over time for analyses of pH, dissolved oxygen and ammonia-N by potentiometric methods. Nitrite (NO_2^- -N), and nitrate (NO_3^- -N) concentrations were determined using a flow injection system (FIAlab-2500). Dissolved sulfide concentrations were estimated by colorimetric assays (APHA, 2012). Gaseous samples were monitored over time in the influent and effluent of the biotrickling filter using a gas analyser (Biogas 5000-Geotech).

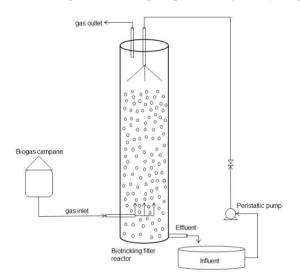


Figure 1. Schematic of a counter-current biotrickling filter.

RESULTS AND DISCUSSION

The biotrickling filter was monitored for over 73 days. Figure 2 shows the concentration profiles of H_2S , CO_2 and CH_4 in the reactor's influent and effluent gas lines over time. H_2S removal efficiency >92 % was rapidly observed since the begining of the experiment, suggesting very short biological acclimation time. H_2S removal efficiency as high as 98% was observed intermittently. Variations in removal efficiency are expected due to inherent fluctuations in H_2S influent concentrations from 1,100 to 3,000 ppmV. Whereas most biofilters use aerobic culturing media or injection of oxygen to promote H_2S aerobic oxidation, in this study, significant removal efficiencies were achieved under anaerobic conditions. Without replacing the culturing media, sulfuric acid concentrations increased in the media and decreased pH to as low as 3.5 (Figure 3). At this low pH, culturing media was replaced since it can affect H_2S removal efficiency (Jaber et al, 2014). Figure 4 shows that when the anoxic conditions were established (DO <0.1 mg.L⁻¹) removal efficiency did not

decrease. The concentration of CO_2 in the gas stream also decreased after the biofilter. Whereas CO_2 was being used as carbon source to H_2S -oxidizers or being removed by dissolution only remains unknown and requires further investigation. Accumulation of a yellowish sludge deposited at the bottom of the culturing media reservoir indicated deposition of elementary sulfur (Figure 5). This was not surprising since trace amounts of oxygen in the nutrient stock solution could promote biological H_2S oxidation to sulfur (Prescott et al., 2003). Moreover, as previously reported, by Rattanapan (2011), in oxygen-limited environments, oxidation may proceed only to elemental sulphur.

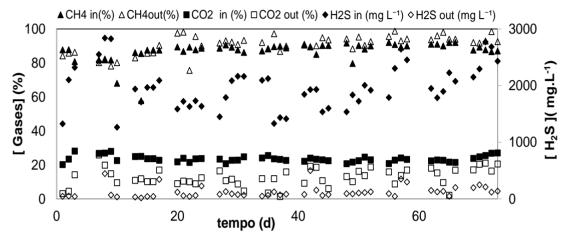
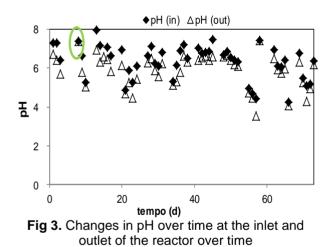


Fig 2. Biotrickling filter evolution over the course of 73 days of monitoring. Inlet and outlet gases concentrations and removal efficiency of hydrogen sulfide



 \diamond OD in (mg L⁻¹) \triangle OD out (mg L⁻¹) δ OD in (mg L⁻¹) \triangle OD out (mg L⁻¹) δ OD in (mg L⁻¹) \triangle OD out (mg L⁻¹) δ OD in (mg L⁻¹) \triangle OD out (mg L⁻¹) δ OD in (mg L⁻¹) \triangle OD out (mg L⁻¹) δ OD in (mg L⁻¹) \triangle OD out (mg L⁻¹) δ OD in (mg L⁻¹) \triangle OD out (mg L⁻¹) δ OD in (mg L⁻¹) \triangle OD out (mg L⁻¹) δ OD in (mg L⁻¹) \triangle OD out (mg L⁻¹) δ OD in (mg L⁻¹) \triangle OD out (mg L⁻¹) δ OD in (mg L⁻¹) \triangle OD out (mg L⁻¹) δ OD in (mg L⁻¹) Δ OD out (mg L⁻¹) δ OD in (mg L⁻¹) Δ OD out (mg L⁻¹) δ OD in (mg L⁻¹) Δ OD out (mg L⁻¹) δ OD in (mg L⁻¹) δ OD out (mg L⁻¹) δ OD in (mg L⁻¹) δ OD out (mg L⁻¹) δ OD in (mg L⁻¹) δ OD out (mg L⁻¹) δ OD in (mg L⁻¹) δ OD out (mg L⁻¹) δ OD in (mg L⁻¹) δ OD out (mg L⁻¹) δ OD in (mg L⁻¹) δ OD out (mg L⁻¹) δ OD in (mg L⁻¹) δ OD out (mg L⁻¹) δ OD in (mg L⁻¹) δ OD out (mg L⁻¹) δ OD in (mg L⁻¹) δ OD out (mg L⁻¹

Fig 4. Dissolved oxygen concentration over time at the inlet and outlet of the reactor.



Fig 5. After a couple days, a clarified nutrient solution showed the presence of a yellowish sludge indicating deposition of elementar sulphur (S₀) in the stock feeding solution reservoir.

CONCLUSIONS

This study demonstrates the efficiency of a field scale anaerobic biofilter to remove H_2S from biogas stream. The time required for reactor's acclimation was negligible. Removal efficiencies as high as 98% were achieved. The system seemed capable of recover elementary sulfur during the biological process. Whether this sulfur can be employed as a valuable fertilizer remains unknown and should be studied further.

ACKNOWLEDGEMENTS

Authors thank financial support from Eletrosul/ ANEEL/ Embrapa Swine and Poultry and Lidimara Suzin grant Nº 1110130054.

REFERENCES

- APHA American Public Health Association. Standard methods for the examination of water and wastewater. 22 ed. 2012 Washington, DC: *American Public Health Association*.
- Abatzoglou, N. S. Boivin, A review of biogas purification processes, Biofuel. Bioprod. Bior. 3 (2009) 42–71.
- Anet, B. M. Lesmale, C. Couriol, T. Lendormi, A. Amrane, P. Le Cloirec, G. Cogny, R. Fillières, Characterization of gaseous odorous emissions from a rendering plant by GC/MS and treatment by biofiltration, J. Environ. Manage. 128 (2013)981–987.
- Kim, M.A. Deshusses, Understanding the limit of H2S degrading biotricklingfilters using a differentia biotrickling filter, Chem. Eng. J. 113 (2005) 119–126.
- Kuai, L., Verstraete, W., 1999. Autotrophic denitrification with elemental Sulphur small-scale wastewater treatment facilities. Environmental Technology 20,201e209.
- Smet, E. P. Lens, H. Van Langenhove, Treatment of waste gases contaminated with odorous sulfur compounds, Crit. Rev. Environ. Sci. Technol. 28 (1998) 89–117.
- Kumar, T.P. M.A.K. Rahul, B. Chandrajit, Biofiltration of volatile organic.Compounds (VOCs) an overview, research, J. Chem. Sci. 1 (2011)
- Prescott, M.L., Harley, P.J., Klein, A.D., 2003. Microbiology, fifth ed. McGraw-Hill Companies, New York, NY83–92.
- Elias, A., Barona, A., Arreguy, A., Rios, J., Aranguiz, I., Peñas, J., 2002. Evaluation of a packing material for the biodegradation of H2S and product analysis. Process Biochemistry 37, 813–820.
- Kim, H., Kim, J.Y., Chung, S.J., Xie, Q., 2002. Long-term operation of a biofilter for simultaneous removal of H2S and NH3. Journal of the Air and Waste Management. Association 52, 1389–1398.
- Sercu, B., Núñez, D., Langenhove, V.H., Aroca, G., Verstraete, W., 2005. Operational and microbiological aspects of a bioaugmented two-stage biotrickling filter removing hydrogen sulfide and dimethyl sulfide. Biotechnology and Bioengineering 90 (2), 259–269.
- Son, Striebig, H-K, B.A., Regan, R.W. 2005. Nutrient Limitations during the Biofiltration of Methyl Isoamyl Ketone. Environmental Prog. 24, 75-81.
- Wani, AH. AK Lau and RMR Branion. Biofiltration control of pulping odors-hydrogen sulfide: performance, macrokinetics and coexistence effects of organo-sulfur species. J. Chem. Technol. Biot. 1999; 74, 9-16.