



III SIMPÓSIO INTERNACIONAL SOBRE GERENCIAMENTO DE
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SULFIDE REMOVAL FROM BIOGAS BY SULFUR-OXIDIZING BACTERIA

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ABSTRACT: The use of renewable biomass-derived biogas methane as source of energy continues receiving special attention worldwide. Prior to its utilization, however, the biogas requires appropriate filtration to minimize the corrosive effects of sulfide on the overall infrastructure. In this work, a lab scale bioreactor inoculated with photosynthetic green sulfur-oxidizing bacteria was evaluated to its potential to remove sulfide. Anaerobic green sulfur-oxidizing bacteria were isolated from a local swine waste pit and induced to grow on a sulfide-rich culturing media. 1-L glass batch reactors were used to mimic the removal of hydrogen sulfide from biogas stream. A negative control inoculated with non-sulfur oxidizing bacteria consortium was used to discern abiotic losses. Removal efficiencies of 100 to 95% were obtained for sulfide concentrations ranging from 610 to 1,200 ppmV, respectively. Interestingly, the prompt sulfide removal rate observed (i.e. < 5 minutes) encouraged further expectations of engineered biofiltering systems to remove sulfide from biogas stream at field scale. Although beyond the scope of this work, the surplus of bacteria biomass produced during the biofiltration process encompasses a source of non-corrosive elementary sulfur that certainly holds promising uses as a valuable fertilizer.

Keywords: biofiltration, biogas, green-sulfur bacteria, sulfide, swine wastewater

INTRODUCTION

The anaerobic biodegradation of agribusiness residues such as animal wastes produces valuable methane as a source of biofuel. Unfortunately, the presence of hydrogen sulfide in the digesters (0.1 to 2%) cause potential problems associated to odor nuisance, health risk and infrastructure corrosion (Roth, 1993; Lastella et al. 2002; Tchobanoglous et al. 2003). Hydrogen sulfide (H₂S) is produced from the degradation of proteins and other sulfur containing compounds present in the organic feed stock. The most common and commercially available technologies to remove H₂S from biogas streams are chemically based and expensive to operate (Gabriel and Deshusses 2003) thereby nullifying at some extent all of the financial benefits associated with potential incomes from energy produced in a cogeneration plant. In Brazil, the use of a less costly and complex to operate iron-based chemical process to filter out sulfide from biogas stream is typically used. Nonetheless, the self-ignitability of the iron sulfide produced during the reaction may pose a potential fire hazardous in these systems. Thus, alternative H₂S removal processes from biogas streams are warrant. Biological treatment processes for the removal of hydrogen sulfide is an attractive alternative to overcome the costly chemical treatment methods. Several studies have discussed on the microbial ecology of phototrophic green sulfur bacteria (GSB) to suitably remove sulfide from biogas stream (Syed et al., 2006). Anaerobic GSB are capable of oxidizing sulfide to elemental sulfur and requires only light, CO₂, and inorganic nutrients for growth. The overall photochemical reaction mediated by GSB was previously described:





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Based on the aforementioned, the objective of this work was twofold: a) isolate indigenous GSB from a local swine waste pit and, b) exploit the biological capabilities of the isolated GSB consortium to effectively remove gaseous sulfide.

MATERIAL AND METHODS

Anaerobic green sulfur-oxidizing bacteria (GSB) were isolated from a local swine waste pit and incubated on Pfennig's modified media (Pfennig, 1974) with 0.0015% yeast at room temperature and under constant illumination with 40W fluorescent lights. A non-sulfur bacteria consortium were grown separately in 1-L glass batch reactors and served to discern sulfide abiotic losses. Each 1-L glass bottle was hermetically closed with a rubber stopper containing two lines to allow liquid and air sample collection.

1 mM Na₂S was added initially and re-spiked at 2 mM to investigate sulfide toxicity potential and the robustness of the biofiltration process. Prior to Na₂S addition the culturing media was purged with nitrogen for 2 min. Sulfide concentrations were collected over time from the reactors headspace using a gas tight syringe and analyzed through colorimetric methylene blue standard test method (ALFAKIT). Photomicrographs of GSB were taken with a Nikon Eclipse E200 microscope equipped with a Moticam 1000 1.3 MP live resolution camera.

RESULTS AND DISCUSSION

The presence of the corrosive sulfide in biogas streams can damage costly infrastructure associated with the conversion of methane into energy by internal combustion engines. Therefore, in this study we investigate the potential of an alternative biological-mediated filtering process to remove gaseous sulfide. Indigenous green sulfur oxidizing bacteria consortium (GSB) was isolated and kept in lab scale bioreactor enriched with sulfide (and resulting dissociated H₂) as a source of electron donor. Headspace sulfide concentrations at 610 ppmV were efficiently removed (100%) by the bacteria within 5 minutes contact time (Figure 1). Additional sulfide was re-spiked into bioreactor at higher concentration (1,220 ppmV) to investigate the robustness of the biological filtering process and the biomass capacity to resist sulfide induced toxicity (Figure 1). Interestingly, GSB were not significantly affected by the high sulfide concentrations tested although a slight decrease in removal rate was observed (95%). Abiotic sulfide losses were negligible as indicated by the absence of sulfide removal in the bioreactor growing non-sulfur bacteria (Figure 1). We recognize that the colorimetric assay utilized in this work was not precisely accurate but provided adequate levels of certainty particularly at the high sulfide concentrations tested.

During the photosynthetic oxidation of sulfide by GSB metabolism, elemental sulfur is excreted from the cells and thus can be further collected and used as a valuable source of fertilizer. Figure 2 shows photomicrographs of the GSB utilized in this work.

CONCLUSIONS

This work was conducted to exploit the possibility of biological sulfide removal from biogas streams through sulfide oxidation to elemental sulfur by a photosynthetic anaerobic bacteria consortium metabolism. GSB isolated from a local swine waste pit were capable of oxidize sulfide anaerobically in the presence of light. The results demonstrated that elevated sulfide concentrations (up to 1220 ppmV) was efficiently removed ($\geq 95\%$) from the lab scale headspace bioreactor at significantly short contact times (≤ 5 min). Whereas



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the exceeding extracellular sulfur produced during a large-scale biofiltering process could serve as a source of sulfur-rich fertilizer remains unclear and warrants further investigation. Overall, the outcomes of this preliminary research clearly demonstrated the promising beneficial aspects of using an engineered biological mediated inline biofiltering process to efficiently remove sulfide from biogas streams.

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REFERENCES

- Gabriel, D. and A.M. Deshusses. 2003. Retrofitting existing chemical scrubbers to biotrickling filters for H₂S emission control. In Proceedings of the National Academy of Science of the United States of America 100(11): 6308–6312.
- Lastella, G., C. Testa, G. Cornacchia, M. Notornicola, F. Voltasio and V.K. Sharma. 2002. Anaerobic digestion of semi-solid organic waste: Biogas production and its purification. Energy Conversion and Management 43: 63-75.
- Pfennig, N. *Rhodopseudomonas globiformis*, sp. n., a new species of the Rhodospirillaceae. Arch. Microbiol., 10 (1974), pp. 197–206.
- Roth, S.H. 1993. Hydrogen sulfide. In Handbook of Hazardous Materials. New York, NY: Academic Press.
- Syed, M., G. Soreanu, P. Falletta and M. Béland (2006). Removal of hydrogen sulfide from gas streams using biological processes - A review. Canadian Biosystems Engineering, 48, 2.1-2.14.
- Tchobanoglous, G., F.L. Burton and H.D. Stensel. 2003. Wastewater Engineering. Treatment and Reuse, 4th edition. McGraw-Hill Companies, New York, NY. Cap. 14: 1505-1532.

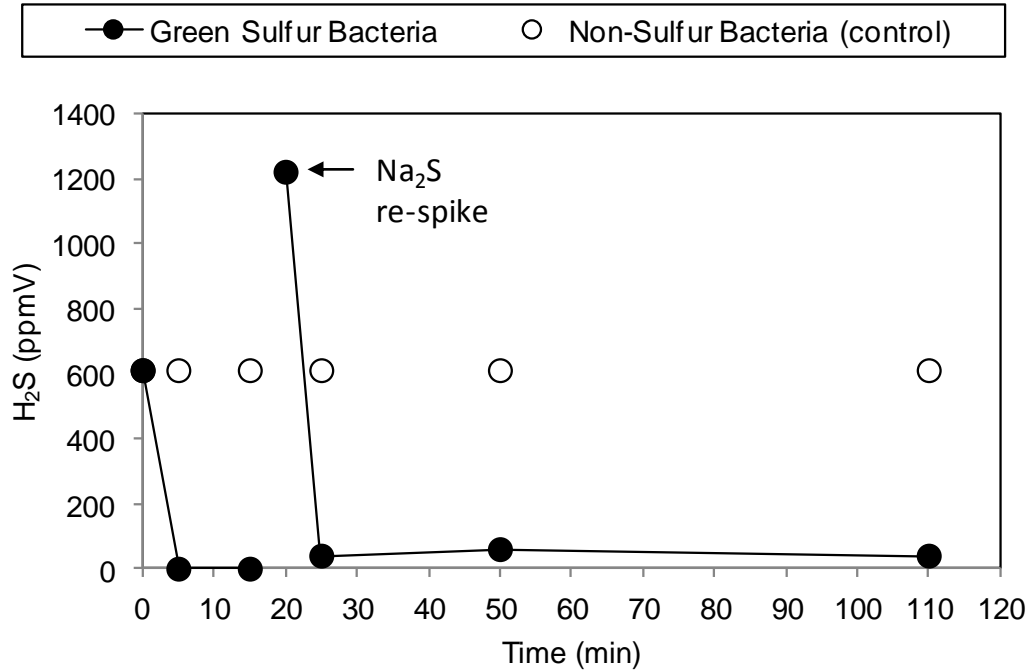


Figure 1. Biological sulfide removal by a green-sulfur bacteria consortium. Sulfide concentration was increased from 610 to 1,200 ppmV to evaluate bacteria resistance to sulfide toxicity. Non-sulfur oxidizing bacteria were utilized as negative control.

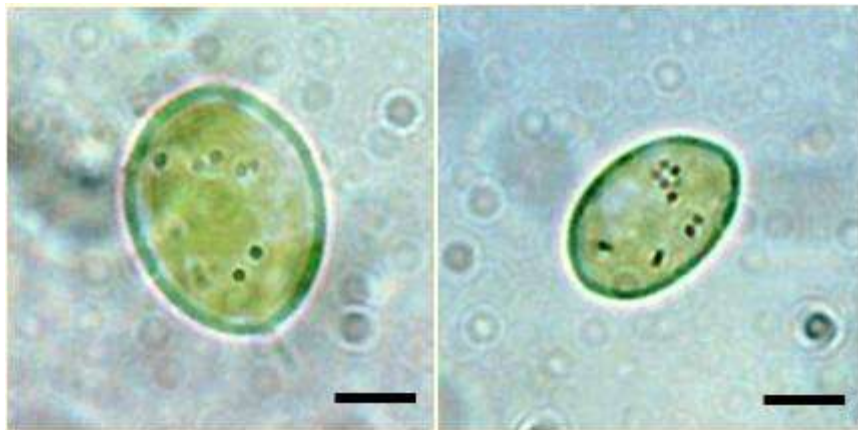


Figure 2. Optical microscopy photographs showing anaerobic photosynthetic green-sulfur bacteria. Scale bar = 0.5 μm .