Sulfide removal from biogas by sulphur-oxidizing bacteria

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Abstract
Biogas methane requires appropriate filtration to minimize the corrosively effects of sulfide on the general infrastructure. In this work, a lab scale bioreactor inoculated with photosynthetic green sulfur-oxidizing bacteria was evaluated to its potential to remove headspace sulfide. Anaerobic green sulfur-oxidizing bacteria were isolated from a local swine waste pit and induced to grow over time 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.

Introduction
The anaerobic biodegradation of agribusiness residues such as swine wastes produces valuable methane as source of biofuel. Hydrogen sulfide is a highly corrosive and odorous compound and unfortunately is present in biogas composition at a concentration of 0.1 to 2% in the digester [1,2]. This compound 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 H_2S from biogas streams are chemically based and expensive to operate [3] 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 chemical process to filter out sulfide from biogas stream using iron particles is typically used. Nonetheless, the self-ignitability of the iron sulfide produced during the reaction may pose a potential fire hazardous in these systems. Therefore, alternative H_2S removal processes from biogas streams are warrant.
Several studies have discussed on the microbial ecology of phototrophic bacteria species of green sulfur bacteria (GSB) to suitably remove sulfide from biogas stream [4]. Anaerobic GSB is capable of oxidizing sulfide to elemental sulfur and requires only light, CO_2, and inorganic nutrients for growth. The overall photochemical reaction mediated by GSB was previously described [5]:

$$2nH_2S + nCO_2 \rightarrow 2nS^0 + n(CH_2O) + nH_2O$$

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
GSB acclimation
Anaerobic green sulfur-oxidizing bacteria (GSB) were isolated from a local swine waste pit and incubated on Pfennig's modified media [6] with 0.0015% yeast at room temperature and under 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.

Biofiltration experiment
1 mM Na_2S was added initially and re-spiked at 2 mM to investigate sulfide toxicity potential and the robustness of the biofiltration process. Prior to Na_2S 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

Biofiltration

The presence of the corrosive sulfide in biogas streams can damage costly infra-structure 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 (1220 ppmV) to investigate the robustness of the biological filtering process and its capacity to resist sulfide induced toxicity (Figure 1). Interestingly, GSB were not significantly affected by the high sulfide concentrations tested although a decrease in removal rates was observed (95%). Abiotic sulfide losses were not likely 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.

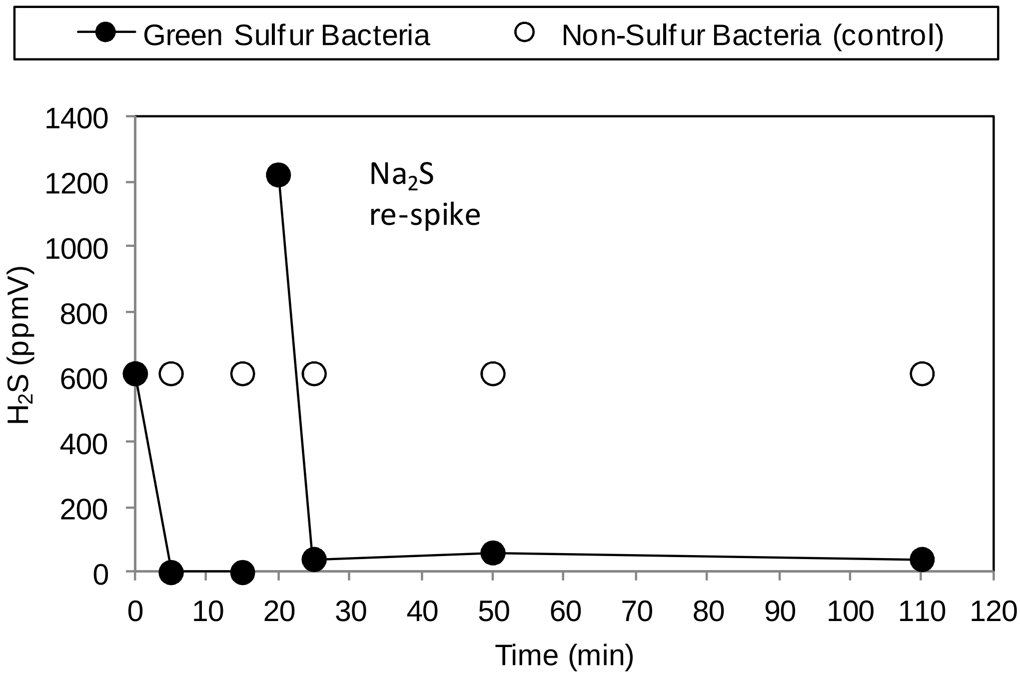

Figure 1. Biological sulfide removal by a green-sulfur bacteria consortium. Sulfide concentration was increased from 610 to 1,200 ppmV to evaluate bacteria resistance to sulfide toxicity. Non-sulfur oxidizing bacteria were utilized as negative control.

Sulfur storage in bacterial cells

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.

Figure 2. Optical microscopy photograph showing green-sulfur bacteria. Scale bar = 0.5 μm.

Conclusion and perspectives

This work was conducted to exploit the possibility of GSB to remove sulfide from biogas streams through sulfide oxidation to elemental sulfur by a photosynthetic anaerobic bacteria consortium metabolism. A GSB capable to oxidize sulfide anaerobically in the presence of light was isolated from a local swine waste pit. The results demonstrated that sulfide concentrations up to 1220 ppmV can be efficiently removed ($\geq$ 95%) biologically from the lab scale headspace bioreactor at significantly short contact times ($\leq$ 5 min). The resulting elementary sulfur produced during sulfide oxidation was stored within the GSB cells. Whereas the exceeding biomass 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 filtering process to efficiently remove sulfide from biogas streams.

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