Cornell University

Dairy Environmental Systems Program

PRO-DAIRY

HYDROGEN SULFIDE REMOVAL FROM BIOGAS

Part 2: Microbial underpinnings of H_2S biological filtration

September 2016

BIOLOGICAL UTILIZATION OF H_2S

Sulfur oxidizing bacteria (SOB) are lithoautotrophs; *lithos* meaning rock or mineral, for their ability to feed on elemental sulfur (S^0); *autotroph* meaning self-feeding, for their ability to produce the complex compounds needed for cell growth [carbohydrates, proteins, fats, nucleic acids] from simple substances [energy from hydrogen sulfide (H_2S) and oxygen (O_2), and carbon from carbon dioxide (CO_2)]. The biological breakdown of H_2S can be described by reactions 1 - 4[1].

$H_2S \leftrightarrow H^+ + HS^-$ (non-biological) (1)

$HS^- + 0.5\ O_2 \rightarrow S^0 + OH^-$ (biological) (2)

$HS^- + 2\ O_2 \rightarrow SO_4^{2-} + H^+$ (biological) (3)

$SO_4^{2-} + H_2O \rightarrow H_2SO_3 + O_2$ (non-biological) (4)

Using biotrickling filters (BTFs) as an example, when O_2 from air is limiting (reaction 2) S^0 is preferentially produced. When O_2 is not limiting (reaction 3) sulfate (SO_4) is preferentially produced. Elemental sulfur will accumulate in a BTFs. This is not ideal and is why the media needs to be removed and cleaned several times a year. Sulfate, however, will dissolve in water and form sulfuric acid (reaction 4), the acid that makes the pH inside a BTFs so low. The formation of the acid is preferred as the dissolved sulfur can be flushed from the BTFs and doesn't accumulate.

Anaerobic biofilters can be designed where SOBs use nitrate (NO_3) instead of O_2 (reactions 5 & 6). As O_2 in air, unlike NO_3-salts, is freely available, anaerobic H_2S removal from biogas is not typically used.

$3H_2S + NO_3^- \rightarrow 3S^0 + 0.5N_2 + 3H_2O$ (biological) (5)

$3H_2S + 4NO_3^- \rightarrow 3SO_4^{2-} + 2N_2 + 6H^+$ (biological) (6)

OPTIMAL SOB GROWTH CONDITIONS

SOB belong to several different groups of bacteria known as genera. These include the *Acidithiobacillus*, *Halothiobacillus*, *Paracoccuc*, *Sulfurimonas*, *Thiobacillus*, and *Thiomonas*. The optimal growth temperatures for these genera are 82-95°F. Most SOB have optimal activities at pH 6-8. At neutral pH, species of *Thiobacillus* are typically dominate in BTFs. Some SOBs have optimal activities under more acidic conditions (pH 2-4). BTFs operated under acidic conditions are typically dominated by species in the genus *Acidithiobacillus* like *Acidithiobacillus thiooxidans* (Figure 1.)[2].

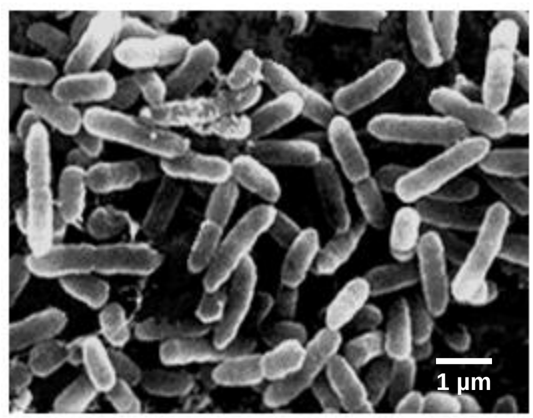

Figure 1. Scanning electron micrograph of *A. thiooxidans*[3].

BIOFILMS

SOB bacteria typically grow as *biofilms*, or aggregations of cells, their metabolites and deposits of their wastes (S^0), attached to the surfaces of BTF media. These biofilms help protect SOB from acidic conditions while providing enhanced surface area for desulfurization. Excessive biofilm growth and the deposition of S^0 can clog BTFs (Figure 2.).

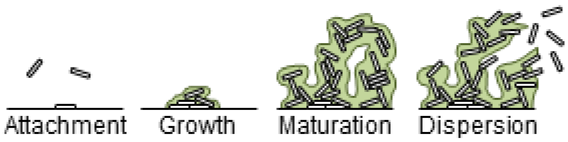

Figure 2. Simplified biofilm growth cycle. The rods represent the SOB, the green represents their metabolites and wastes. Note how the cells are embedded in the biofilm and how this growth form can increase surface area.

SOB Inoculations & Microbial Community Interactions

Biotrickling filters are typically inoculated with SOB to reduce start-up time. Systems can be inoculated with manure and activated sludge, but typically specially developed bacterial cultures are used. As BTF are non-sterile and each has a unique environment, the SOB community will typically shift and deviate from the inoculum. This is dictated by both system operating conditions and microbial interactions. *It is advisable to collect a tote of the liquid trickling-phase from BTFs which is enriched in the system's unique SOB community prior to cleaning media, and use this to re-seed your BTF system after cleaning.*

In counter-flow BTFs where biogas and the trickling-phase are opposite, most H_2S elimination occurs in the lower portion of the reactor where biogas and O_2 are loaded. SO_4 is also preferentially produced here due to high O_2 supply, while S^0 formation is more prevalent in the upper portions of the system. In BTFs where flow is co-current with the trickling-phase, most H_2S elimination occurs in the upper portion of the reactor with S^0 formation more prevalent in the lower portions of the system. SOB communities are recognized to partition in biogas desulfurization systems along these concentration gradients[4].

Improved knowledge of the microbial interactions in BTFs and their responses to operational conditions could support the development of 1) inoculations that speed the establishment of an active microbial consortium, 2) selection methods for robust hydrogen sulfide reducing capacities, and 3) optimizations that limit the formation of S^0 and biofilm clogging. In the meantime, BTF are successfully managed to ensure H_2S reductions by using regular tower flushing, media backwashing, and re-seeding with collected trickling-phase after cleaning.

Fact Sheet Series

Hydrogen Sulfide Removal from Biogas

Part 1: Available technologies for hydrogen sulfide removal from biogas
Part 2: Microbial underpinnings of H_2S biological filtration
Part 3: Biotrickling filters for H_2S - Overview of configuration and design
Part 4: Biotrickling filters for H_2S - Improvement opportunities

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References

[1] Muñoz R, Meir L, Diaz I, and Jeison D. 2015. A review on the state-of-the-art of physical/chemical and biological technologies for biogas upgrading. *Reviews in Environmental Science and Biotechnology* 14:727-759. **[2]** Montebello AM, Bezerra T, Rovira R, Rago L, Lafuente J, Gamisans X, Campoy S, Baeza M, and Gabriel D. 2013. Operational aspects, pH transition and microbial shifts of a H_2S desulfurizing biotrickling filter with random packing material. *Chemosphere* 93:2675-2682. **[3]** Khan S, Haq F, Hasan F, Saeed K & Ullah R. 2012. Growth and biochemical activities of *Acidithiobacillus thiooxidans* collected from black shale. *Journal of Microbiology Research* 2(4):78-83. **[4]** Montebello AM, Mora M, López LR, Bezerra T, Gamisans X, Lafuente J, Baeza M & Gabriel D. 2014. Aerobic desulfurization of biogas by acidic biotrickling filtration in a randomly packed reactor. *Journal of Hazardous Materials*. 280:200-208.