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Micro-aeration for hydrogen sulfide removal from biogas

by

Thanapong Duangmanee

A dissertation submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Co-majors: Civil Engineering (Environmental Engineering); Biorenewable Resources and Technology

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2009

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ABSTRACT

The presence of sulfur compounds (e.g. protein, sulfate, thiosulfate, sulfite, etc.) in the feed stream generates highly corrosive and odorous hydrogen sulfide during anaerobic digestion. The high sulfide level in the biogas stream is not only poisonous to many novel metal catalysts employed in thermo-catalytic processes but also reduces the quality of methane to produce renewable energy. This study used an innovative, low-maintenance, low-cost biological sulfide removal technology to remove sulfides simultaneously from both gas and liquid phase. ORP (Oxidation-Reduction-Potential) was used as the controlling parameter to precisely regulate air injection to the sulfide oxidizing unit (SOU). The micro-aeration technique provided just enough oxygen to partially oxidize sulfides to elemental sulfur without inhibiting methanogenesis. The SOU was equipped with a diffuser at the bottom for the dispersion of sulfide-laden biogas and injected air throughout the column. The SOU can be operated as a standalone unit or coupled with an anaerobic digester to simultaneously remove sulfide from the biogas and effluent.

The integrated system was capable of reducing hydrogen sulfide in biogas from 2,450 to less than 2 ppmV with minimal sulfate production at the highest available sulfide loading rate of 0.24 kg/m^3-day. More than 98% of sulfide removed was recovered as elemental sulfur. However, the standalone SOU was able to operate at high hydrogen sulfide loading of 1.46 kg/m^3-day at inlet sulfide concentration of 3000 ppmV and reduce the off-gas hydrogen sulfide concentrations to less than 10 ppmV. The experiment also revealed that the ORP controlled aeration was sensitive enough to prevent oxygen overdosing (dampening effect) during unexpected surges of aeration. Using generalized linear regression, a model

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predicting output H_2S concentration based on input H_2S concentrations, SOU medium heights, and biogas flow rates, was derived. With 95% confidence, output H_2S concentration was affected by changes in liquid heights the most, followed by changes in flow rates.

Feasibility studies for H_2S removal from biogas by micro-aeration were conducted at the Ames Water Pollution Control Facility (AWPCF) by using different types of liquid media available at the plant, i.e. plant effluent, mixed liquor, and digester supernatant. From the experiment at AWPCF, it was found that operating pHs were affected by the amount of alkalinity in the liquid media and that the removal efficiencies were affected by the operating pH. Among all the liquid media tested, digester supernatant showed the greatest potential with more than 99% H_2S removal at an operating pH of 7.0 and volumetric biogas flow rate of 21.6 m^3/m^3-hr. By increasing trace metal contents and temperature of the medium, the hydrogen sulfide removal rate was greatly improved. The operating cost of the full-scale system was estimated to be approximately $2/kg-S-removed. In addition, it was also revealed that abiotic sulfide oxidation accounted for 95% of overall sulfide oxidation.

This technology is expected to widen the use of biogas as a renewable fuel since the maintenance requirements of biogas handling equipment, the methane purification costs, and the emissions of SOx will dramatically be reduced. Importantly, the technology does not require inoculation of special bacteria, addition of nutrients and trace elements, or chemicals for pH control.

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CHAPTER 1. GENERAL INTRODUCTION

Introduction

Anaerobic treatment of high sulfate/protein waste streams, e.g. animal wastes, contributes several different types of sulfur-containing compounds, including hydrogen sulfide, mercaptans, etc. The sulfur-containing compounds are not only malodorous and harmful but also hinder the use of biogas as a renewable energy source in downstream processes, such as in boilers for heating, internal combustion engines for electricity production, and catalytic processes for methanol and biodiesel production.

Previous studies have proven that sulfide could be biologically or chemically converted to elemental sulfur. The major drawbacks for biological processes include the need for nutrients to support microorganism growth and the sustainability of the process. Even though the chemical process can solve some of these issues, it is more expensive and creates disposal problems.

In practical application, sulfide generation is associated with anaerobic treatment of sulfate/protein-rich waste streams, which contain sufficient nutrients to support the growth of both methane production and sulfide oxidizing bacteria. As a result, the use of anaerobic digester effluent as a medium in an integrated methane production/sulfide oxidizing system and a standalone sulfide removal system may help to reduce the overall cost of hydrogen sulfide removal. In addition, the sulfide concentration in the effluent from the sulfide oxidizing unit (SOU) would be so low that the odor potential can be minimized. To remove hydrogen sulfide in the integrated system, a portion of sulfide-free biogas produced from the

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SOU is recycled back to the anaerobic digester to provide digester mixing and, at the same time, to strip newly formed hydrogen sulfide in the digester to be treated in the SOU. If a standalone sulfide removal system is desired, all biogas is dosed with a small quantity of air before passing through the SOU.

For operation control, precise oxygen dosing is extremely important to selectively convert the sulfide to elemental sulfur and to minimize the carry over of oxygen to the anaerobic digester. Oxygen introduced into the digester may reduce the methane yield (in the case of an integrated system) or end up in the biogas and form an explosive mixture of methane and oxygen. Oxidation-reduction potential (ORP) will be used as a controlling parameter to precisely regulate oxygen dosing for hydrogen sulfide conversion to elemental sulfur. Either too much or too little oxygen will lead to sulfate formation or sulfide residual in the biogas, respectively. In addition, most sulfide control studies have been conducted using packed media in a tower to facilitate the conversion to elemental sulfur. However, the use of media is not applicable for treating wastewater with a high solid content due to media clogging potential. Therefore, the proposed study will employ a specially designed tubular oxidation reactor, the SOU, without packing media.

To produce sulfide-free biogas, a low-cost, easy-to-operate, hydrogen sulfide oxidation unit has been developed. The unit can be integrated into an anaerobic digester or operated as a standalone system. The coupling of the SOU with the anaerobic digester allows (1) the SOU to use the effluent of anaerobic digester as medium and nutrient supplement for sulfide removal and (2) hydrogen sulfide to be stripped off from the content of anaerobic digester as soon as it is produced. The system employs ORP as a parameter to control the degree of air injection and sulfide oxidation toward elemental sulfur recovery.

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The specific aims of the proposed study included the following:

1) To develop a low cost, easy-to-operate, ORP-based sulfide oxidation system for sulfide-free biogas production from an anaerobic digester treating high-solid wastewater,
2) To study the mechanisms involved in sulfide oxidation in a reactor system,
3) To examine the sulfide removal efficiency of the system at various operating conditions (sulfide loading rate, biogas recirculation rate, and pH) with different liquid media in the SOU, and
4) To develop design criteria for full-scale operations.

Dissertation Organization

The dissertation is organized into three main parts—general introduction and literature review, experiment, and general conclusion. The experiment part consisted of three research papers, describing studies at the Environmental Research Lab at Iowa State University and at the City of Ames Water Pollution Control Facility. Thanapong Duangmanee was the primary author and data collector of all three papers.

Literature Review

Anaerobic digestion is one of the methods for producing biorenewable energy (Brown, 2003; Syed *et al.*, 2006). Biorenewable energy is, by definition, the energy produced from renewable resources, the resources that can regenerate themselves within a few years. By being able to regenerate themselves in a relatively shot time, it is certain that the resources will be available all the time, aka "sustainable resources." Since substrates of

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the anaerobic digestion are usually from agricultural origins that will be available all the time as long as humans raise animals and/or grow plants, anaerobic digestion is undoubtedly a method to produce sustainable energy for the future.

When wastes containing protein, sulfate, or other oxidized forms of sulfur are fed to the digester, sulfate reducing bacteria (SRB), such as *Desulfovibrio, Desulfotomaculum, Desulfobacter, Desulfosarcina, and Desulfococcus*, will reduce sulfur containing compounds to sulfides (Clanton and Schmidt, 2000), resulting in biogas contaminated with hydrogen sulfide (Eq. 1).

$$SO_4^{2-} + \text{Organic matter} \rightarrow HS^- + H_2O + HCO_3^- \qquad \text{Eq. 1}$$

The hydrogen sulfide in biogas limits the usage of biogas in many down stream processes. For instance, heat production using boilers requires hydrogen sulfide to be less than 1000 ppmV whereas hydrogen sulfide limitations in electricity production by internal combustion engine is only 100 ppmV (Zicari, 2003). If biogas is to be used as natural gas, the hydrogen sulfide needs to be less than 4 ppmV (Amirfakhri *et al.*, 2006; Sublette and Sylvester, 1987a). Some other novel catalytic processes to convert methane to methanol as a feedstock for other chemical production, such as the production of biodiesel, require no presence of hydrogen sulfide.

Methods to remove sulfide from biogas include (1) chemical processes, (2) physicochemical processes, and (3) biological processes.

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Chemical processes for hydrogen sulfide removal

In chemical processes, chemicals are added into liquids containing sulfides to either oxidize sulfides or to shift volatile sulfide, hydrogen sulfide, to the nonvolatile ones. According to Eqs 2 to 4, adding base into the solution would transform hydrogen sulfide to bisulfide and sulfide, preventing odorous sulfide from vaporizing.

$$H_2S_{gas} \leftrightarrow H_2S_{aq} \qquad \text{Eq. 2}$$

$$H_2S_{aq} \leftrightarrow HS^- + H^+ \qquad \text{Eq. 3}$$

$$HS^- \leftrightarrow S^{2-} + H^+ \qquad \text{Eq. 4}$$

At 25 °C and pH of 7, if hydrogen sulfide in a vessel headspace is 3700 ppmV, at pH of 8, the concentration will be 830 ppmV, and at pH of 10, the concentration in headspace will be reduced to 10 ppmV. Adding base solution may help to reduce hydrogen sulfide, but, at pH above 8, anaerobic digestion will be inhibited. Oxidizing agents, such as chlorine, can be used to oxidize sulfide (Droste, 1997). Besides chlorine, other oxidizing agents, such as ozone, potassium permanganate, hydrogen peroxide, and nitrite, can be used. The dosage of the oxidizing agents can be problematic since not only do the agents oxidize sulfide, but also oxidize other organic and inorganic compounds present in wastewater. Adding chlorine or nitrite in wastewater produces unwanted byproducts, such as carcinogenic trihalomethane (THM), NOx, and ammonia (Droste, 1997; Kohl and Neilsen, 1997).

$$H_2S + NaNO_2 \leftrightarrow NH_3 + 3S^0 + NaOH + \text{some } NO_x \qquad \text{Eq. 5}$$

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Physicochemical processes for hydrogen sulfide removal

In physicochemical processes, solid or liquid chemicals react with hydrogen sulfide in gas phase through either adsorption or absorption mechanisms. The physical interaction of the chemicals and hydrogen sulfide is provided through a bubbling column, spray tower, trickling column, or other column-like container.

Solid adsorbents: Iron oxide is one of the solid chemicals used to remove hydrogen sulfide from biogas (Kohl and Neilsen, 1997). The famous one is "iron sponge." To remove hydrogen sulfide, dirty gas is forced to a container or a series of containers filled with iron sponge. The iron oxide of iron sponge reacts with hydrogen sulfide and mercaptans (Eqs. 6 and 7), and the spent iron sponge can be regenerated by blowing air into the containers (Eq 8).

$$2Fe_2O_3 + 6H_2S \leftrightarrow 2Fe_2S_3 + 6H_2O \qquad \text{Eq 6.}$$

$$2Fe_2O_3 + 6RSH \leftrightarrow 2Fe(RS)_3 + 3H_2O \qquad \text{Eq 7.}$$

$$2Fe_2S_3 + 3O_2 \leftrightarrow 2Fe_2O_3 + 6S \qquad \text{Eq 8.}$$

For every lb of ferric oxide, 0.64 lb of hydrogen sulfide can be removed if hydrogen sulfide is completely transformed to iron sulfide. For it to be effective, the iron oxide needs to be in true hydrated form, not just wetted iron oxide. The regenerative reaction of iron oxide is highly exothermic; great care should be taken when it is conducted (Kohl and Neilsen, 1997). However, after every regeneration, the iron sponge will lose approximately 30% of its activity due to clogging by elemental sulfur and loss of hydrated water from the

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iron sponge; therefore, a new sponge is needed after two to three regeneration (Zicari, 2003), making it useful only for just small volume of gas purification.

Impregnated carbon is also widely used in gaseous hydrogen sulfide removal processes. The technique offers the combined effect of adsorption and chemical reaction. A carbon source, such as wood chips, serves as an adsorbent for hydrogen sulfide. Reactive chemicals, such as metal oxide (iron or zinc) and alkaline materials (sodium hydroxide or sodium carbonate), react with the sulfide and hold it in place as metal sulfide or sulfate (Eqs. 9 and 10).

$$ZnO + H_2S \leftrightarrow ZnS + H_2O \qquad \text{Eq. 9}$$

$$2NaOH + H_2S \leftrightarrow Na_2S + 2H_2O \qquad \text{Eq. 10}$$

This combination increases the overall efficiency of the adsorbent. The impregnated carbon is best to remove trace amounts of hydrogen sulfide, other low molecular-weight sulfur compounds, and some volatile organic compounds. In addition, if an iron oxide bed is used, sodium carbonate should be added to the bed to control the pH between 8 and 10 (Kohl and Neilsen, 1997).

Liquid absorbents: Using liquid absorbent to remove hydrogen sulfide has increasingly become popular in natural gas purification. With just a couple of vertical bubbling columns (contactors), the liquid process can be installed in a small foot-print. Regenerative capability of the absorbent in the process provides reduced labor costs since the process can be operated in a continuous mode—absorption of sulfide and regeneration of absorbent. More importantly, elemental sulfur produced in the process can be recovered

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relatively easily, compared to that in a solid adsorbent process. Some of the liquid media include iron oxide slurries, zinc oxide slurries, oxidizing solutions, aldehydes, alkylamine/aldehyde condensation products, triazines (polyamine), and caustic solutions (Kohl and Neilsen, 1997). The iron oxide slurries, aka *Slurrisweet process*, has a similar chemistry as that of iron sponge. The advantage is the ease of replacing and removing the spent media. The *Chemsweet process* uses powders of zinc oxide and zinc acetate mixed with water to dissolve hydrogen sulfide and precipitate out as zinc sulfide (Eqs. 11 to 13). During operation, the pH of the media must be kept low to avoid carbon dioxide absorption but kept high enough to prevent corrosion.

$$ZnAc + H_2S \leftrightarrow ZnS + 2HAc \qquad \text{Eq 11.}$$

$$ZnO + 2HAC \leftrightarrow ZnAc + 2H_2O \qquad \text{Eq 12.}$$

$$\text{Overall:} \quad ZnO + H_2S \leftrightarrow ZnS + 2H_2O \qquad \text{Eq 13.}$$

Trace amount of hydrogen sulfide can be removed by using oxidizing solutions, such as permanganate and dichromate solutions. The process consists of two bubbling columns operating in series, filled with 4% of permanganate or 5-10% of dichromate as the main ingredients. When 75% of the oxidizing solution is used, it must be replaced. In the *Sulfa-Check* and *Hondo HS-100 processes*, nitrite solutions (either potassium or sodium) are used to absorb hydrogen sulfide and convert it into elemental sulfur (Eq. 5). Even though the removal process can be achieved in just a single bubbling column, the solutions cannot be regenerated. They have to be discarded and replaced with fresh solutions after all active nitrite is consumed.

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Aldehyde is very reactive with hydrogen sulfide. In the aldehyde process, such as the *Scavinox process*, the aldehyde absorbent is a mixture of formaldehyde and methanol. After reacting with hydrogen sulfide, the resulting products are cyclic carbon-sulfur and small amounts of mercaptans. Even though this process is very effective, the reaction reactants and products have a very strong offensive odor and disposal of the spent solutions is a major problem. For these reasons, the process is not widely used today.

Hydrogen sulfide is readily absorbed in alkali solutionsas in the caustic scrubbing process. To prevent carbon dioxide from absorbing into the solution, the retention time needs to be short. In a single stage, hydrogen sulfide can be reduced from 7,500 to 600 ppm, which may be clean enough for some uses (Kohl and Neilsen, 1997). Although disposal of the spent solution may be problematic in some cases, some reaction products, such as sodium bisulfide (NaHS), can still be used in paper manufacture.

Even though chemical and physiochemical processes seem to be very effective in removing hydrogen sulfide from biogas, the processes present unavoidable problems, such as high capital, labor, energy, and chemical costs (Buisman *et al.*, 1991). Disposal of the spent chemicals presents a major additional problem of the processes. As an alternative, biological processes can convert hydrogen sulfide to elemental sulfur or sulfate with minimal use of energy. Not only do the processes eliminate the generation of toxic wastes, they do not require the use of any catalyst, except for small amounts of oxygen, nutrients, and/or light.

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***Biological processes* for hydrogen sulfide removal**

Microorganisms responsible for hydrogen sulfide removal fall into one of the three categories—purple sulfur bacteria, green sulfur bacteria, and colorless sulfur bacteria (Robertson and Kuenen, 2001; Madigan and Martinko, 2005). Syed *et al*. (2006) summarized the biological processes to remove hydrogen sulfide from gas streams.

Being part of proteobacteria, purple sulfur bacteria are a group of facultative bacteria capable of oxidizing sulfide to elemental sulfur in the presence of light. The purple sulfur bacteria are classified into two families according to the location of sulfur deposited—Chromatiaceae (i.e. genus *Chromatium*) and Ectothiorhodospiraceae (i.e. genus *Ectothio-rhodospira*), which deposit sulfur outside and inside their cells, respectively. Green sulfur bacteria represent a group of obligate phototrophic, strict anaerobes that use sulfide as an electron donor and convert it to elemental sulfur, which is deposited outside their cells. Representative of this group is the genus *Chlorobium* (family Chlorobiaceae). The conversion of sulfide to elemental sulfur follows Van Niel's reaction (Eq. 14):

$$2nH_2S + nCO_2 \xrightarrow{hv} 2nS + n(CH_2O) + nH_2O \qquad \text{Eq. 14}$$

The colorless sulfur bacteria consist of very diverse bacterial groups that can oxidize reduced sulfur (sulfide, elemental sulfur, thiosulfate, or organic sulfur) to gain energy and support growth. Besides reduced sulfur compounds, some groups of bacteria can use ferrous ion as an electron donor. While a majority of the colorless sulfur bacteria use oxygen as an electron acceptor, some can use nitrate in the process known as denitrification (Robertson

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and Kuenen, 2001;). Among the colorless bacteria studied, *Thiobacillus* appears in research papers the most frequently. Common reactions of this group of bacteria are the followings:

$$2HS^- + 4O_2 \rightarrow 2SO_4^{2-} + 2H^+ \qquad \Delta G^{0'} = -732.58 \text{ kJ/mol} \qquad \text{Eq. 15}$$

$$2HS^- + O_2 \rightarrow 2S^0 + 2OH^- \qquad \Delta G^{0'} = -129.50 \text{ kJ/mol} \qquad \text{Eq. 16}$$

$$2S^0 + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 \qquad \Delta G^{0'} = -563.23 \text{kJ/mol} \qquad \text{Eq. 17}$$

$$S_2O_3^{2-} + 2O_2 + H_2O \leftrightarrow SO_4^{2-} + H_2SO_4 \qquad \text{Eq. 18}$$

$$5H_2S + 8NO_3^- \rightarrow 4SO_4^{2-} + H_2SO_4 + 4N_2 + H_2O \qquad \text{Eq. 19}$$

$$5H_2S + 2NO_3^- \rightarrow 5S^0 + N_2 + 2OH^- + 4H_2O \qquad \text{Eq. 20}$$

$$5S^0 + 6NO_3^- + 2H_2O \rightarrow 3SO_4^{2-} + 2H_2SO_4 + 3N_2 \qquad \text{Eq. 21}$$

Phototrophic bacteria: Phototrophic green and purple bacteria can be found in almost any water body, especially on the surface of the water that has been polluted with organic materials and exposed to sunlight (Siefert *et al.*, 1978). They have bacteriophyll that can capture light energy at 460 to 760 nm and use it for sulfide oxidation. The challenges for sulfide removal using phototrophic sulfur bacteria include (1) the reactor design that allows light penetration and (2) the amount of energy required. The degree of sulfide conversion to elemental sulfur or to sulfate depends on the amount of light the bacteria received. In a simple CSTR reactor with a fixed light intensity, it was found that at a sulfide loading rate of 2.1 mg/L-hr in liquid, almost all of the sulfide was oxidized to sulfate. At a loading of 4.4 mg/L-hr, complete conversion of sulfide to elemental sulfur was achieved. However, at the loading rate of 5.6 mg/L-hr, sulfide was found accumulated in a reactor (Henshaw *et al.*, 1998). With nutrient supplement, *Chlorobium thiosulfatophilum*, a green sulfur bacteria, was

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successfully used to remove hydrogen sulfide from gas containing as much as 3.6% hydrogen sulfide using a very complex 15-L reactor equipped with a light collecting system that can harvest light from either the sun or a 400 W light bulb (An and Kim, 2000). The delivery of light into the reactor was achieved by using scratched optical fibers for dispersion of light along the wall of the fiber. The fibers were covered with glass enclosure to prevent the solids from attaching on the surface. The authors tried to use sunlight to save energy; however, they found that, when only sunlight was used, the sulfide removal rate was about four times less than that when the light bulb was used, stating the significance of the continuity of the light source. Henshaw and Zhu (2001) used a pure culture, fixed-film, multiple-tubular reactor to increase surface area exposed to light. A 250 W infrared bulb was used as a light source. Among many loading rates tested (111 to 328 mg/L-hr), complete sulfide removal was found at a sulfide loading rate of 286 mg/L-hr with 92-95% elemental sulfur recovery. It can be seen that when using the phototrophic sulfur bacteria to remove sulfide, the reactor must be optimized to obtain the maximum light exposure, in terms of reactor design and cleaning. To remove sulfide as elemental sulfur, light intensity needs to be optimized. In addition, supplemental nutrients are also required.

Colorless sulfur bacteria: The majority of hydrogen sulfide removal research has focused on using colorless sulfur bacteria. The bacteria may be in suspension or attached to plastic or organic media. Chemoautotrophic bacteria, such as *Thiobacillus*, have been used to remove hydrogen sulfide from a gas stream. Gadre (1989) used a fixed-film reactor inoculated with an enriched culture of *Thiobacillus* to remove hydrogen sulfide from biogas containing as much as 2.4% (v/v) of hydrogen sulfide. The biogas was generated from an anaerobic filter used to treat high-sulfate sugarcane molasses distillery wastewater. The

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reactor was supplied with a nutrient solution to support the growth of the autotrophic bacteria. In the exhaust gas, the hydrogen sulfide content was found to be on the average of 0.62% with overall removal efficiency, elemental sulfur recovery, and volumetric efficiency of 70%, 20%, and 3.2 mmol H_2S removal /L-hr, respectively. Buisman *et al.* (1991) used a Rotating Biological Contactor (RBC) sulfide treatment system to remove sulfide from sulfide-containing anaerobically treated papermill wastewater (30-150 mg-S^{2-}/L). To control the oxygen percentage in the headspace, the headspace volume of the reactor was exchanged with a different rate of flowing air (20% of oxygen in the headspace could be satisfied by an air flow rate of 22 L-air/min). It was found that more than 90% of the sulfide was removed in effluent at an HRT of 19 min. However, the exhaust gas from the reactor still contained as high as 1,500 ppm of hydrogen sulfide, which required further treatment. A novel full-scale biogas purification process was adopted by Nishimura and Yoda (1997). The process integrated an UASB reactor and activated sludge (AS) process with a multiple-tray contact tower. Mixed liquor was trickled from the top of the tower while biogas was blown upwards from the bottom of the tower. Sulfide containing mixed liquor was dropped into an aeration tank where the sulfide was oxidized into sulfate. Hydrogen sulfide in the biogas was reduced from approximately 2,000 ppm to about 20 ppm at the biogas flow rate of 40 m^3/hr. However, the process design did not allow for elemental sulfur recovery.

The use of a pure culture, *Thiobacillus thiooxidans,* has been conducted by Ranade and Bhirangi (2001). The culture was allowed to grow in a fixed-film reactor with a nutrient medium pumped from a reservoir into the top of reactor and exiting at the bottom, dropping once again into the reservoir. The author claimed that the biogas coming out from the reactor was free from hydrogen sulfide and that the optimum sulfide loading rate was 2.03 kg-

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H_2S/m^3-day (2.49 mmol-H_2S/L-hr). A similar set up was found to remove 98% hydrogen sulfide from a gas stream containing hydrogen sulfide as small as 20-100 ppmV by bacterial isolate *Acinetogacter* sp. MU1_03 and *Alcaligenes faecalis* MU2_03 (Potivichayanon *et al*., 2006). It also found that improvement of hydrogen sulfide removal efficiency could be obtained from increasing gas retention time, liquid flow rate, and column height.

A biofilter filled with organic media, such as soil, compost, peat, woodchips or any combination thereof, is one of the most cost effective methods to remove low levels of hydrogen sulfide and other volatile organic compounds (VOCs). The biofilter can also be augmented with microorganisms to increase its hydrogen sulfide removing efficiency. Chung *et al.* (1996) used a biofilter filled with immobilized *Thiobacillus thioparus* CH11 in Ca-alginate and found that more than 98% of hydrogen sulfide could be removed at a hydrogen sulfide loading rate of 25 g/m^3-hr. Ammonia and hydrogen sulfide can be removed simultaneously with a biofilter filled with woodchips. 85% and 90% removal efficiencies were obtained when a biofilter was used to treat gas with 100 and 80 ppmV of hydrogen sulfide and ammonia, respectively (Jones *et al*., 2004). Elias *et al.* (2002) used a pelletized mixture of pig manure and sawdust packed in a lab-scale biofilter and found that 90% of 170 ppmV of hydrogen sulfide could be removed when a superficial gas flow rate was 200 m/hr.

In 1987ab, Sublette and Sylvester conducted several experiments on desulfurization of natural gas using *Thiobacillus denitrificans*. It was found that the microorganism could use sulfide as an energy source and reduce hydrogen sulfide to very low levels in a reactor operated under a sulfide-limiting condition (< 200 μM or 6.4 mg/L as S). The microorganism can tolerate high pressure (up to 12.5 MPa) well, but has a narrow range of optimum growth temperature (around 30 °C). Contamination by heterotrophs did not show

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any effect on sulfide reduction, which made it possible for aseptic operation. Using the same microorganism, 10% of hydrogen sulfide in synthetic biogas can be reduced to undetectable levels with 1-2 seconds of gas contact time in a bubbling column. However, since the authors used an airflow rate almost twice that of biogas, the entire product is sulfate (Sublettle *et al*., 1994). Amirfakhri *et al*. (2006) proposed the use of autotrophic denitrification to replace the aeration step (for regeneration) in the *Seaboard process*, a natural gas desulfurization process which uses sodium carbonate to absorb hydrogen sulfide. The aeration step usually introduced a side reaction and disposal problem of foul air containing hydrogen sulfide. In the autotrophic denitrification, thiosulfate or sulfide is used as an electron donor (energy source) while nitrate and carbon dioxide is used as an electron acceptor and carbon source, respectively. With added nitrate, the process occurred in five-compartmentalized anaerobic baffled reactors (ABR) that received a sulfide loading rate of0.62 mmole/L-hr. Since sulfide was completely oxidized in the first compartment, the overall removal rate was 3.03 mmole/L-hr (96 mg-S/L-hr). However, only 61% of sulfide was converted to elemental sulfur. An innovative process was proposed by Kleerebezem and Mendez (2002) to treat high-organic, high-sulfate wastewater, such as that from fish processing industries. The process consisted of an anaerobic digester to convert organic matter and sulfate to hydrogen sulfide containing biogas with ammonium discharged in the effluent. The ammonium was converted to nitrate in an aeration tank. The effluent from the aeration tank was sprayed in an absorption column to absorb hydrogen sulfide from biogas produced from the anaerobic digester. Nitrate and sulfide containing effluent was then fed to an autotrophic denitrification fixed-film reactor to produce nitrogen and sulfate. However, the author only focused on the fixed-film part with nitrate being overdosed, which resulted in

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complete oxidation of sulfide. The author also mentioned that a higher oxidation rate was not achieved since the filter was clogged with elemental sulfur.

Other methods can be employed to indirectly remove hydrogen sulfide from biogas using a combination of chemical and biological processes. Fe(III) can oxidize hydrogen sulfide to elemental sulfur. The reduced Fe(II) can then be oxidized by iron-oxidizing bacteria, such as *T. ferrooxidans, Acidithiobacillus ferrooxidans,* and *Leptospirillum ferrooxidans*. The process can occur simultaneously in one reactor or occur in separate reactors with an improved sulfide removal efficiency (Park *et al*., 2005; Son and Lee, 2005).

Oxygen in anaerobic digestion

In anaerobic digestion, oxygen has been believed to be a toxic substance to the anaerobic consortium. However, in some circumstances, limited amounts of oxygen may be beneficial, especially in the removal of hydrogen sulfide. To remove small amounts of hydrogen sulfide in biogas, a small amount of air can be injected into the anaerobic digester at a rate of 7.5% of biogas production, which can reduce hydrogen sulfide from about 680 to less than 10 ppmV (Ikbal *et al*., 2003). For anaerobic treatment of high sulfate and high COD wastewater, high levels of sulfide would be present in liquid and gas phases, which may pose a threat to the methanogenesis process. In a wastewater with 1200 mg-SO_4^{2-}/L (the condition that otherwise inhibits methanogenesis), introduction of a limited amount of aeration directly into a fluidized-bed anaerobic digester showed 60% improvement in terms of COD removal with a four-fold higher methane production (Zitomer and Shrout, 2000).

In biological sulfide removal from gas or liquid streams, elemental sulfur is the preferred final product (Janssen *et al*., 1997; Janssen et *al*., 1998). Since elemental sulfur is

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insoluble, it can be removed from the streams relatively easily, resulting in reducing the overall sulfur species. Sulfide oxidation to elemental sulfur requires four times less oxygen than the oxidation to sulfate; therefore, the energy consumption through aeration can greatly be reduced. To gear the biological sulfide oxidation to sulfur formation, the supply of oxygen needs to be optimized. By monitoring and controlling the molar ratio of oxygen/sulfide consumption (O_2/S^{2-}) in a biological sulfide oxidizing reactor, at steady state, it was found that the maximum elemental sulfur formation occurred at O_2/S^{2-} of 0.6 to 1.0, not at 0.5 as suggested by Eq. 16 (Janssen *et al*., 1995). A similar result was obtained by Alcantara *et al.* (2004) who used a different strain of *Thiobacillus* sp. They found the O_2/S^{2-} of 0.5 yielded the most sulfur. When O_2/S^{2-} was more than 1.0, sulfate was a major, if not only, product of the sulfide oxidation. In 0.3 to 0.7 range of O_2/S^{2-}, thiosulfate also formed, which was believed to be through chemical auto-oxidation (Eq. 22).

$$2HS^- + 2O_2 \rightarrow H_2O + S_2O_3^{2-} \qquad \text{Eq. 22}$$

Oxidation-reduction potential

Oxidation-Reduction Potential (ORP) or Redox potential signifies the tendency of a given solution to gain or lose electrons (Sawyer *et al*., 2003). It is a measurement of the ratio of oxidized-to-reduced forms of all chemical species in the solution. Oxidizing compounds have the ability to accept the electrons while reducing compounds have the ability to donate electrons. The ORP electrode measures the electron activities. According to the Nernst half-cell potential equation ($ox + ne^- \rightarrow red$), the measured ORP is defined as:

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$$E_h = E^0 + (\frac{2.303RT}{nF})\log\frac{\{ox\}}{\{red\}} \qquad \text{Eq. 23}$$

where E_h = measured ORP (mV), E^0 = standard electrode potential, R = the gas constant (8.314 J/K-mol), T = temperature (K), n = the number of electrons involved, F = the Faraday's constant = 95,000 coulombs/mol, and {ox} or {red} = activity of oxidants and reductants, respectively. A negative ORP indicates the tendency of the solution to donate electrons to the electrode (reducing environment), while a solution with positive ORP indicates its ability to accept electrons from the electrode (oxidizing environment). However, the ORP is usually referenced with standard hydrogen electrode (SHE). The ORP with respect to SHE can be calculated by:

$$E = E_h + E_{Ref} \qquad \text{Eq. 24}$$

where E_{Ref} = electrode potential with respect to SHE (mv)

pH affects the ORP when the reaction contains H^+. Formation of $H_2S_{(g)}$ can be derived from two half-cell reactions:

$$S_{(s)} + 2H^+ + 2e^- \rightarrow H_2S_{(g)} \qquad E^0 = 0.141 \text{ volt} \qquad \text{Eq. 25}$$

$$S^{2-} \rightarrow S_{(s)} + 2e^- \qquad E^0 = 0.48 \text{ volt} \qquad \text{Eq. 26}$$

Net $$S^{2-} + 2H^+ \leftrightarrow H_2S_{(g)} \qquad E^0 = 0.621 \text{ volt} \qquad \text{Eq. 27}$$

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A positive E^0 indicates that the reaction can theoretically proceed as written. Considering Eq 25, the Nernst half-cell equation suggests the inverse relationship between ORP and pH as the following:.

$$E = E^0 + (\frac{2.303RT}{nF})\log\frac{[S_{(s)}][H^+]^2}{[H_2S_{(g)}]} \qquad \text{Eq. 28}$$

$$E = E^0 - (\frac{2.303RT}{F})pH + (\frac{2.303RT}{2F})\log\frac{[S_{(s)}]}{[H_2S_{(g)}]} \qquad \text{Eq. 29}$$

Beside pH, ORP is also affected by the change in temperature. However, the effect of temperature to ORP is rather complex since the temperature affects the electrode itself as well as it affects ionic activities of chemicals in the solution. Therefore, it is preferable that the reaction is carried out at constant temperature and pH.

Application of oxidation-reduction potential

The ORP has been used for "real time" monitoring and control of critical disinfectant levels in water disinfection (Suslow, 2004). The ORP measurement can define the antimicrobial potential regardless of water quality (e.g. pH) when hypochlorite is used as a disinfectant. The effectiveness of disinfection depends on availability of pH-dependent chlorine species. Hypochlorous acid (HOCl) is more effective than hypochlorite ion (OCl^-). As pH rises, the proportion of HOCl decreases and more chlorine is needed to maintain the same effectiveness of disinfection This can be achieved by maintaining the same ORP

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level—"an ORP of 700 mV at pH 6.5 has the same killing potential as the same ORP at pH 8.5". The application of ORP can also be extended to wastewater treatment when it is critical to control the amount of aeration. To reduce the high cost of aeration and alkalinity addition for nitrification/denitrification processes , partial oxidation of ammonia to nitrite, followed by autotrophic ammonia oxidation (anammox) was introduced (Ganigaué *et al*., 2007). The critical component of this process is the partial oxidation of ammonia to nitrite so that the 1:1 ratio of ammonia to nitrite is maintained (Eq. 30) for the anammox reaction.

$$NH_4^+ + 2HCO_3^- + 1.5O_2 \rightarrow NO_2^- + 3H_2O + 2CO_2 \qquad \text{Eq. 30}$$

The ORP could also be utilized as a controlling parameter in aerobic/anoxic processes for carbon and nitrogen removal in a sequencing batch reactor (SBR). The rapid changes in ORP would signal the end of each process in the reactor, allowing for better control of the system (Puig *et al*., 2005).

Oxidation-reduction potential in sulfide removal

During sulfur formation, dissolved oxygen never exceeds 0.1 mg/L, resulting in difficult oxygen input control into the reactor; therefore, a better controlling parameter needs to be developed to maximize sulfide oxidation to elemental sulfur. Janssen *et al*. (1995) demonstrated a linear relationship between ORP and the logarithm of sulfide concentration. Later in 1998, Janssen *et al*. successfully demonstrated the use of oxidation-reduction potential (ORP) to control O_2/S^{2-} to approximately 0.38 while the amount of sulfide loading rate was varied simultaneously. By controlling ORP at -137 mV, elemental sulfur was found

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to be a major product, accounting for over 80% of total sulfide loaded. However, Krishnakumar *et al.* (2005) used a similar reactor set up to find optimal ORP to maximize elemental sulfur production and found that an ORP range of -400 to -300 mV contributed around 80% sulfur recovery when the reactor was loaded by 19 kg-S^{2-}/m^3-day. Sulfide was nearly 100% removed with sulfate and thiosulfate as the rest of the oxidizing products. Khanal and Huang (2003b) have conducted experiments to verify the feasibility of using ORP as the controlling parameter for oxygen injection to an upflow anaerobic filter treating high sulfate and COD wastewater. By setting operating ORP at 25 mV above natural ORP (-300 to -290 mV) in otherwise inhibitory influent sulfate concentrations (6000 mg/L), sulfide was reduced to only 12 mg/L with an improvement of methane generation by 46%.

Oxidation of sulfide to elemental sulfur is faster than the oxidation to sulfate (Janssen *et al*., 1995). Therefore, it is possible to prevent sulfur from being oxidized to sulfate (Eqs. 17 and 20). This can be achieved by the removal of formed sulfur as soon as possible via better reactor design (Janssen *et al*., 1997; Krishnakumar *et al*., 2005)

Most of the research mentioned above has focused on using the treatment of soluble wastewater. Little attention has been paid to high-solids content wastewaters, such as animal waste (Total Soilds, TS of 2-6%). The use of packed media in an anaerobic digester or in a sulfide oxidizing reactor simply prevents them from treating high-solid wastes due to clogging potential. Since the proposed system does not require nutrient addition, pH adjustment, or media, the integration of the SOU and anaerobic digester will offer a low-cost, easy-to-operate, alternative for removing sulfide from gas and/or liquid streams. The only requirement is limited air addition that is precisely controlled by ORP. The circulation of sulfide-free biogas back to the anaerobic digester will remove newly formed sulfide as

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quickly as it is produced. However, when the integration is not preferred, the SOU can also be operated as a standalone unit, appended to existing biogas generating facilities with little modification.

This innovative sulfide removal system is expected to be upgradable to full-scale in municipal, agricultural, and industrial applications.

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MICRO-AERATION FOR SULFIDE REMOVAL IN ANAEROBIC TREATMENT OF HIGH-SOLID WASTEWATER: A PILOT-SCALE STUDY

A paper to be submitted to *Water Environmental Research*

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ABSTRACT

The presence of sulfur compounds (e.g. protein, sulfate, thiosulfate, sulfite, etc.) in the feed stream generates highly corrosive and odorous hydrogen sulfide during anaerobic digestion. The high sulfide levels in the biogas stream are not only poisonous to many novel metal catalysts employed in thermo-catalytic processes but also reduce the quality of methane as a renewable energy source. This study used an innovative, low-maintenance, low-cost biological sulfide removal technology to remove sulfides simultaneously from both gas and liquid phase. ORP (Oxidation-Reduction-Potential) was used as the controlling parameter to precisely regulate air injection to the sulfide oxidizing unit attached to the digester. The micro-aeration technique provided just enough oxygen to partially oxidize sulfides to elemental sulfur without inhibiting methanogenesis. The integrated system was capable of reducing hydrogen sulfide in biogas from 2,450 to less than 2 ppmV with minimal sulfate production. More than 98% of sulfide removed was recovered as elemental sulfur. This technology will widen the use of biogas as a renewable

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fuel since the maintenance requirement of downstream processes, the biogas purification cost, and the emission of SO_x in the off-gas will dramatically be reduced. Importantly, the technology does not require inoculation of special bacteria, addition of nutrients and trace elements, or pH control.

KEYWORDS

Biological sulfide removal, anaerobic digester, ORP, micro-aeration, hydrogen sulfide

INTRODUCTION

Anaerobic processes have been widely adopted to stabilize wastes/wastewater due to several inherent attributes, such as the generation of renewable energy (methane), less sludge production, lower energy consumption than aerobic counter part, etc. However, the presence of sulfur compounds (e.g. protein, sulfate, thiosulfate, sulfite, etc.) in the feed stream generates highly corrosive and odorous hydrogen sulfide during anaerobic treatment. The high sulfide level in the biogas stream is not only poisonous to many novel metal catalysts employed in thermo-catalytic processes; but also reduces the quality of methane as a renewable energy. Moreover, aqueous sulfide in the bioreactor has a potential to inhibit methanogenesis, the main pathway for methane production in anaerobic processes. This significantly reduces the methane yield (Khanal *et al.*, 2003).

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When wastes containing sulfur compounds are fed to the digester, sulfate reducing bacteria (SRB), such as *Desulfovibrio, Desulfotomaculum, Desulfobacter, Desulfosarcina, and Desulfococcus*, will reduce sulfur containing compounds to sulfides (Clanton and Schmidt, 2000), resulting in biogas contaminated with hydrogen sulfide by the following equations:

$$SO_4^{2-} + \text{Organic matter} \rightarrow HS^- + H_2O + HCO_3^-$$

$$HS^- + H^+ \leftrightarrow H_2S_{(g)}$$

The hydrogen sulfide in biogas limits the usage of biogas in many down stream processes. For instance, heat production using a boiler requires hydrogen sulfide to be less than 1000 ppmV whereas the hydrogen sulfide limitation in electricity production by internal combustion engine is only 100 ppmV (Zicari, 2003). To inject methane generated from a digester into a pipeline, hydrogen sulfide concentration is required to be less than 4 ppmV. Some other novel catalytic processes to convert methane into other useful ingredients(such as biodiesel) require no presence of hydrogen sulfide. In addition, burning biogas containing hydrogen sulfide would produce sulfur oxides, which is a main precursor of acid rain.. In addition to hydrogen sulfide in the off-gas, sulfides in liquid phase, if they are allowed to release to the receiving steam, will be toxic to aquatic life and deplete oxygen concentrations.

Methods to remove hydrogen sulfide from the biogas stream consist of mainly chemical, physical and/or biological processes. Chemical processes involve adding chemicals into liquids containing sulfides to either oxidize the sulfides or shift volatile sulfides (hydrogen sulfide) to

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the nonvolatile ones (sulfide and bisulfide). Such chemicals are alkaline solutions, chlorine, ozone, potassium permanganate, hydrogen peroxide, and nitrite. However, the dosage of the oxidizing agents can be problematic since not only do these agents oxidize sulfide, but also oxidize other organic and inorganic compounds present in wastewater. Adding chlorine or nitrite in wastewater produces unwanted byproducts, such as carcinogenic trihalomethane (THM), NOx, and ammonia. Physical processes involve the use of metal oxides (e.g. iron and zinc oxides), alkaline solutions, zinc acetate, ferrous chloride molecular sieve, activated carbon, etc. to react with sulfide. However, these processes are high-cost and have inherent chemical disposal problems. The sulfide removal activity deteriorates over a short period of time unless the absorbents are replaced, which incur recurring expenses. In addition, the precipitates formed may greatly reduce the active volume of the digester (Droste, 1997, Kohl and Neilsen, 1997). Biological processes involve utilizing aerobic chemoautotrophs or anaerobic photoautotrophs to oxidize sulfides in both gas and liquid phases to elemental sulfur (Henshaw et al., 1998). The sulfide removal rates of the biological processes are comparable to that of the chemical or physical processes. Moreover, biologically-produced sulfur is known as a better substrate for bioleaching of heavy metal contaminated wastes, such as swine manure (Tichý, 1994).

Even though biological sulfide removal by anaerobic photoautotrophs is promising, it has two major disadvantages—the need for light and a complex reactor design. Sulfide removal by aerobic chemoautotrophs offers a much easier reactor design with a high sulfide removal rate. Among the aerobic chemoautotroph studied, *Thiobacillus* is the most prevalent in research papers (Syed *et al.,* 2006). The following equations depict some biological sulfide removal processes:

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$$2HS^- + 4O_2 \rightarrow 2SO_4^{2-} + 2H^+ \qquad \Delta G^{0'} = -732.58 \text{ kJ/mol}$$

$$2HS^- + O_2 \rightarrow 2S^0 + 2OH^- \qquad \Delta G^{0'} = -129.50 \text{ kJ/mol}$$

$$2S^0 + 3O_2 + 2H_2O \rightarrow 2H_2SO_4$$

$$S_2O_3^{2-} + 2O_2 + H_2O \leftrightarrow SO_4^{2-} + H_2SO_4$$

In biological sulfide removal from gas or liquid streams, elemental sulfur is preferred as a final product (Janssen *et al.*, 1997 and 1998). Since elemental sulfur is insoluble, it can be removed from the streams relatively easy, which results in the reduction of overall sulfur species. Sulfide oxidation to elemental sulfur requires four times less oxygen than the oxidation to sulfate; therefore, the energy consumption through aeration can greatly be reduced. To gear the biological sulfide oxidation to sulfur formation, the supply of oxygen needs to be optimized. If the molar ratio of oxygen/sulfide consumption (O_2/S^{2-}) is at 2 or more, sulfate will be the major product. However, if the O_2/S^{2-} ratio is approximately 0.5, then the majority of the products will be elemental sulfur. By monitoring and controlling the molar ratio of oxygen/sulfide consumption (O_2/S^{2-}) in a biological sulfide oxidizing reactor, at steady state, it was found that the maximum elemental sulfur formation occurred at O_2/S^{2-} of 0.6 to 1.0, not at 0.5 (Janssen *et al.*, 1995). A similar result was obtained by Alcantara *et al.* (2004) who used a different strain of *Thiobacillus* sp., but they found the $O_2/S^{2-}$of 0.5 yielded the most sulfur. Oxidation of sulfide to elemental sulfur is faster than the oxidation to sulfate (Janssen *et al.*, 1995). Therefore, it is possible to prevent sulfur from being oxidized to sulfate. This can be achieved by the removal of formed sulfur as soon as possible via improved reactor design (Janssen *et al.*, 1997, Krishnakumar *et al.*, 2005). When O_2/S^{2-} was more than 1.0, sulfate was a major, if not the only,

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product of sulfide oxidation. In the 0.3 to 0.7 range of O_2/S^{2-}, thiosulfate also formed, which was believed to be through chemical auto-oxidation as the following reaction:

$$2HS^- + 2O_2 \rightarrow H_2O + S_2O_3^{2-}$$

During sulfur formation, dissolved oxygen never exceeded 0.1 mg/L, making oxygen input into the reactor difficult to control. Janssen *et al.* (1998) successfully demonstrated the use of oxidation-reduction potential (ORP) to control O_2/S^{2-} to approximately 0.38 while the sulfide loading rate was varied simultaneously. By controlling ORP at -137 mV, elemental sulfur was found to be a major product, accounting for over 80% of total sulfide loaded. However, Krishnakumar *et al.* (2005) used a similar reactor set up to find the optimal ORP to maximize elemental sulfur production and found that an ORP range of -400 to -300 mV contributed around 80% sulfur recovery when the reactor was loaded at 19 kg-S^{2-}/m^3-day. Sulfide was nearly 100% removed with sulfate and thiosulfate as the oxidizing products. Khanal and Huang (2003) have conducted experiments to verify the feasibility of using ORP as the controlling parameter for oxygen injection into an upflow anaerobic filter treating high sulfate and COD wastewater. By setting operating ORP at 25 mV above natural ORP (-300 to -290 mV) in otherwise inhibitory influent sulfate concentration (6000 mg/L), sulfide was reduced to only 12 mg/L with an improvement of methane generation by 46%.

Most of the previously research mentioned has focused on using the treatment of dilute wastewater. Little attention has been paid to high-solids wastewater treatment, such as animal waste (TS of 2-6%). The use of packed media in an anaerobic digester or in a sulfide oxidizing

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reactor prevents them from treating high-solids waste due to the potential for clogging. In this research, a low-cost, simultaneous, complete sulfide removal method from both gas and liquid phases was used, using an integrated sulfide oxidation reactor connected to an anaerobic digester treating high solid wastes. Because the sulfide oxidizing unit (SOU) was not filled with packing media, the SOU was able to cope with a much higher solids concentration than other sulfur oxidizing columns (Krishnakumar *et al.,* 2005, Khanal *et al.*, 2003, Koe and Fang, 2000). Since the integration did not require nutrients, trace element addition, or pH adjustment, it offered considerable advantages over typical biological sulfide removal systems. The only requirement is limited air addition whose amount is controlled by an ORP set point, on-off aeration, or continuous air injection. This innovative sulfide removal and sulfur recovery system is expected to be upgradeable to full-scale in municipal, agricultural, and industrial applications.

The objective of this research was to evaluate the feasibility of using the integrated system to remove hydrogen sulfide from biogas with maximum sulfur recovery but minimal sulfate production. The performances of the digester and SOU before and after aeration were compared. The mass balance of sulfur species (including sulfate, thiosulfate, sulfide, and elemental sulfur) was conducted. In addition, the activities of methanogens, sulfate reducing bacteria, and facultative bacteria towards the overall treatment process were investigated.

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METHODOLOGY

Integrated sulfide removal systems

Figure 1 shows a pilot-scale facility. The system consisted of a one-liter sulfide oxidizing unit (SOU) integrated with an anaerobic digester, a continuous stirred tank reactor (CSTR) with an internal settling zone, that had a working volume of 92 L. The effluent from the digester was pumped out of the system into the SOU to provide medium for sulfide removal.

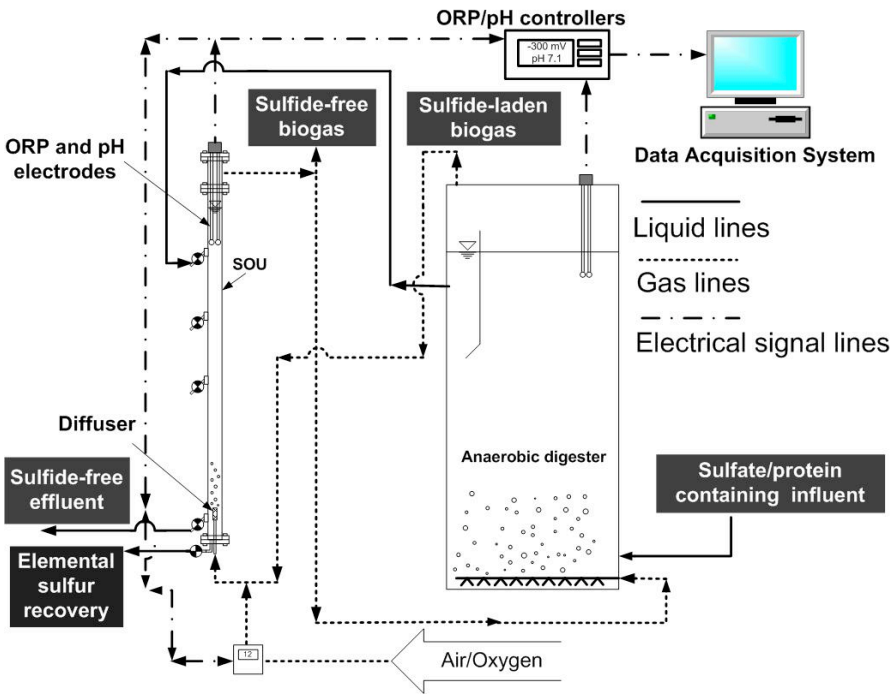

Figure 1 – Schematic of the sulfide removing system.

Sulfide-laden biogas produced in the digester was mixed with a small amount of air before being

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forced through a diffuser located at the bottom of the SOU. In the SOU, sulfide and oxygen flowed upward in a countercurrent direction against the digester effluent, where the formation of elemental sulfur took place. The produced elemental sulfur was collected in the bottom of the SOU and discharged periodically. Sulfide-free biogas was re-circulated back to the digester to scavenge the newly formed sulfide and brought back to the SOU again. The cycle was repeated. Hydraulic retention times (HRTs) of the pilot scale digester and the SOU were controlled at 20 days and 4 hrs, respectively. The digester was continuously mixed by means of biogas recirculation at the rate of 1.5 L/min (0.016 $L/L_{digester}$-min) whereas the biogas recirculation rate of the SOU was 0.5 L/min (0.5 L/L_{sou}-min). The integrated system was operated at a room temperature of 25±2°C. The organic loading and COD rate to the digester were approximately 0.8 g-VS/L-day and 1.2 g-COD/L-day, respectively (Table 1).

Table 1 – The chemical analysis of the substrate.

Parameters	
TS, g/L	21.1 ± 2.4
VS, g/L	15.5 ± 1.5
Alkalinity, g/L as $CaCO_3$	1.3 ± 0.3
pH	6.5 ± 0.7
TCOD, g/L	24.2 ± 2.5
SCOD, g/L	3.4 ± 0.6
SO_4, mg/L	122 ± 8
Sulfides, mg/L	ND[1]
$S_2O_3^{2-}$, mg/L	ND

ND = Not detected

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Aeration control: Two sets of pH and ORP probes were installed on top of the digester and SOU. Every minute, the ORP/pH controller received signals from the ORP and pH electrodes in the SOU and responded to the changes of the ORP. Depending on the ORP set point, the controller either turned ON or OFF a solenoid valve that would OPEN (injecting air) or CLOSE (stop injecting air), respectively. The actual airflow into the SOU was also monitored with a flow meter. A computer was used as a data acquisition system for monitoring and recording various necessary outputs. During the beginning of the study, the aeration was controlled by ORP set points. However, later on, a continuous aeration method (5 ml/min) was used and the corresponding ORP reading was monitored.

Startup: The digester was inoculated with anaerobic digester sludge from a local wastewater treatment plant and fed with a synthetic organic substrate. Fifteen liters of the synthetic organic substrate consisted of 338.1 g of commercial dog food (with minimum 27% of crude protein, minimum of 15% crude fat , maximum of 4% crude fiber, maximum 4% of moisture by weight), 50 g of $NaHCO_3$, and 15 ml of a trace element solution (prepared by adding 10 g of $FeCl_2.4H_2O$, 2.0 g of $CoCl_2.6H_2O$, 1.0 g of EDTA, 500 mg of $MnCl_2.4H_2O$, 200 mg of Resazurin, 142 mg of $NiCl_2.6H_2O$, 123 mg of Na_2SeO_3, 90 mg of $AlCl_3.6H_2O$, 50 mg of H_3BO_3, 50 mg of $ZnCl_2$, 50 mg of $(NH_4)_6MoO_{24}.4H_2O$, 38 mg of $CuCl_2.2H_2O$, and 1.0 ml of HCl (37.7% solution) into distilled water to make 1 liter). Substrate preparation was conducted by soaking the dog food for 1 day, adding $NaHCO_3$ and the trace element solution, and adjusting the volume to 15 L by tap water. The substrate was kept in a 4°C refrigerator prior to feeding. Table 1 shows the chemical analysis of the substrate.

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Steady state operation: After more than six months after digester start up, the SOU was connected to the digester as shown in Figure 1. The testing of the integrated system was not conducted until the system was in a steady state, which was approximately three months (three HRTs of the digester) after the startup. After all experiments under a no-aeration condition were completed, the system was subjected to aeration for sulfide removal. The testing of the system under an aeration condition was not conducted until another steady state was reached, which was approximately another three-month period.

Batch experiments

Biomass preparation: Three batch experiments (methanogenic /sulfidogenic activity and specific oxygen uptake rate tests) were conducted. The biomass was obtained by using a tube attached between the effluent port of the SOU and a bottle that had been flushed with 60:40% of N_2/CO_2 gas mixture to simulate the condition found in the integrated system. To minimize the exposure to oxygen in the air, biomass from the digester was taken just before the experiment. Regardless of where the biomass came from, the biomass concentration in batch bottles was set to 2 and 1 g-VS/L for methanogenic/sufidogenic activity and specific oxygen uptake rate tests, respectively. To achieve the desired biomass concentration in each bottle, an appropriated amount of reactor content was centrifuged at 3600 x *g*. After discarding the supernatant, the biomass was then mixed with the appropriate amount of nutrient solution [prepared by adding 7.95g of $NaH_2PO_4.H_2O$, 6.0 g of K_2HPO_4, 2.8 g of NH_4Cl, 1.0 g of $MgSO_4.7H_2O$, 1.0 g of Yeast extracts, 0.1 g of $CaCl_2$, and 10 ml of trace element solution (above) into deoxygenated distilled water to make 1 liter], resuspended using a vortex mixer, and inoculated into each bottle.

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Methanogenic activities. The specific methanogenic activity tests (SMA) were conducted by using either 250-ml or 500-ml batch bottles with an active volume of 150 ml (total volumes of 280 and 610 ml, respectively). For methanogenic activity tests using acetate or glucose as a substrate, the 250-ml serum bottles were inoculated with concentrated biomass mixed with 15 ml of nutrient solution, acetate or glucose (2.0 g COD/L in the bottles), alkalinity (3.3 g/L as $CaCO_3$ in the bottles), and deoxygenated distilled water to make 150 ml. After adjusting the pH to 7.0, the bottles were flushed with 80:20% of N_2/CO_2 gas mixture and capped with rubber septas. For methanogenic activity tests using hydrogen as a substrate, the 500-ml serum bottles were inoculated with the same amount of chemicals and biomass as in the methanogenic activity tests without adding glucose or sodium acetate. After adjusting the pH to 7.0, the bottles were flushed with 80:20% of H_2/CO_2 gas mixture, capped with rubber septas, and injected with 128 ml of 80:20% of H_2/CO_2 gas mixture to result in 2 g COD/L (or 0.3 g COD) in the bottles. All the bottles were incubated at room temperature (25 ± 2°C) on a shaker table rotating at 180 rpm. All the experiments were duplicated.

Methane production estimation: For bottles using acetate and glucose as a substrate, biogas production and methane concentration was measured periodically using a wetted syringe and a gas chromatograph, respectively. To estimate the amount of methane production, the following equation was used:

$$\text{Methane production (ml)} = \frac{[(M_1V_1) + (M_1V_H) - (M_0V_H)}{100}$$

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where M_1 and M_0 = methane concentration at the current time and at the previous time, respectively; V_1 = volumetric biogas production; V_H = head space volume of the serum bottle, which is equal to 130 ml.

For bottles using hydrogen as substrate, after the pressure in bottles became negative, N_2 was injected into bottles until the pressure was equal to atmosphere. The methane concentration was then measured, and the methane production was estimated using the following equation:

$$\text{Methane production (ml)} = \frac{[(M_1V_H) + (M_0V_H)}{100}$$

where V_H = head space volume of the serum bottle, which is equal to 460 ml. When the bottles had positive pressure, the first equation to estimate methane production was used. The cumulative methane productions were plotted against experimental time, and the methane production rate was estimated from the highest slope.

Sulfidogenic activities: The sulfidogenic activity tests (SA) were conducted the same way as methanogenic activity except K_2SO_4 (3.0 g/L in the bottles) and Bromoethane sulfonic acid (BES), 98% (50 mM in the bottles) were added into the bottles as a source of sulfate and methane inhibitor, respectively. Sodium acetate, glucose, or hydrogen was used as a substrate (2 g COD/L in the bottles). The COD/SO_4^{2-} ratio in each bottle was set at 0.67 to minimize the methanogenic activity (Patidar and Tare, 2004). Periodically, samples were taken from the bottles to measure sulfate concentrations. The sulfate reduction rate was estimated from the

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highest slope. For all the experiments, duplicates were used.

Specific oxygen uptake rate: The specific oxygen uptake rate (SOUR) was conducted using BOD bottles with an active volume of 300 ml. The bottles were inoculated with concentrated biomass mixed with 30 ml of nutrient solution, glucose (1.0 g COD/L in the bottles), alkalinity (0.8 g/L as $CaCO_3$ in the bottles), and aerated distilled water to make 300 ml. After adjusting the pH to 7.0, a dissolved oxygen (DO) probe was mounted on each bottle. The depletion of the DO concentration was measured every minute to estimate SOUR. Duplicates were used for all experiments.

Analytical methods

Methane, carbon dioxide, and nitrogen in the biogas were analyzed with a Gow Mac series 350 GC-TCD fitted with an 84-mm (3.3-in.) stainless-steel column packed with Porapak T (60/80 mesh) (GOW-MAC Instrument Company, Bethlehem, PA, USA). Helium was used as the carrier gas at a flowrate of 35 mL/min. The temperatures of the injection port, oven, and detector were at 150, 50, and 100°C, respectively. Oxygen and hydrogen sulfide in the biogas were analyzed with a Gow Mac series 400 GC-TCD fitted with Chromosil '310 and Molesieve 18 80/100 (8 ft) column. Helium was used as the carrier gas at a flow rate of 30 ml/min. The temperatures of the injection port, oven, and detector were at 100, 60, and 115°C, respectively. Hydrogen sulfide was also measured by a BW defender multi-gas detector (D4-2002) and Draeger tubes (RAE system). All gas production data reported were standardized to standard temperature (0°C) and pressure (760 mm Hg). Sulfate and thiosulfate were analyzed by ion chromatograph (Dionex

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model DX 500, Dionex Cooperation, Sunnyvale, CA, USA) with AN1 anionic column and ASRS® ULTRA II, 4 mm, suppressor (Dionex P/N 061561) at 50 mA suppressor conductivity. Sodium carbonate/biocarbonate eluent (1.8/1.7 mmole/L) was used as the mobile phase at conductivity at a flow rate of 1 ml/min. Volatile fatty acids (VFAs), Total solids (TS), Volatile solids (VS), aqueous sulfide, alkalinity, and COD measurements were made in accordance with the procedures listed in Standard Methods (APHA *et al.,* 1995). Elemental sulfur was quantified by a mass balance approach (Krishanakumar *et al.,* 2005). The soluble COD (SCOD) was defined as the COD component that passed through a 0.45-μm pore size filter. pH and ORP was monitored through a pH/ORP controller (Consort R305, Consort nv, Belgium).

RESULTS AND DISCUSSION

Continuous experiments

Micro-aeration experiment: In the beginning of the micro-aeration period of the continuous experiment, the aeration rate was arbitrarily set at 7 ml/min with an ORP set point of -210 mV. Figure 2 shows ORP and H_2S profiles of the SOU and digester during the beginning of the micro-aeration period. The numbers beside the data points represent hydrogen sulfide concentrations.

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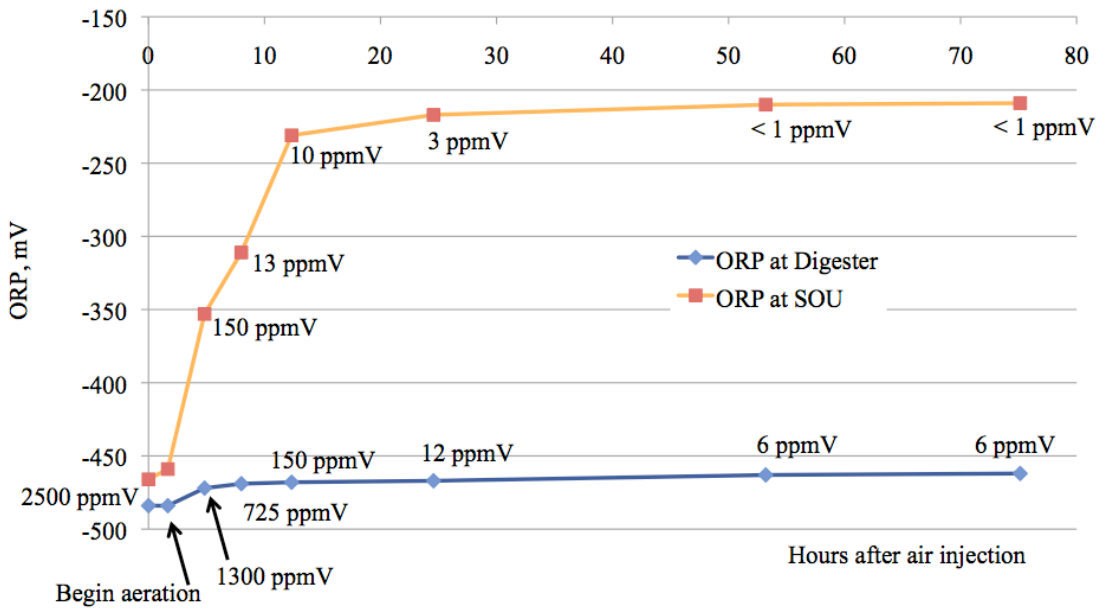

Figure 2 – ORP and H_2S profiles during the beginning of the micro-aeration period.

It took merely 24 hours to reduce the hydrogen sulfide in the biogas at the one-liter SOU from 2500 to 3 ppmV and to less than 1 ppmV by the following day. The ORP of the SOU increased from -462 mV to the set point ORP of -210 mV. However, the ORP of the digester only went up 22 mV from -484 mV.

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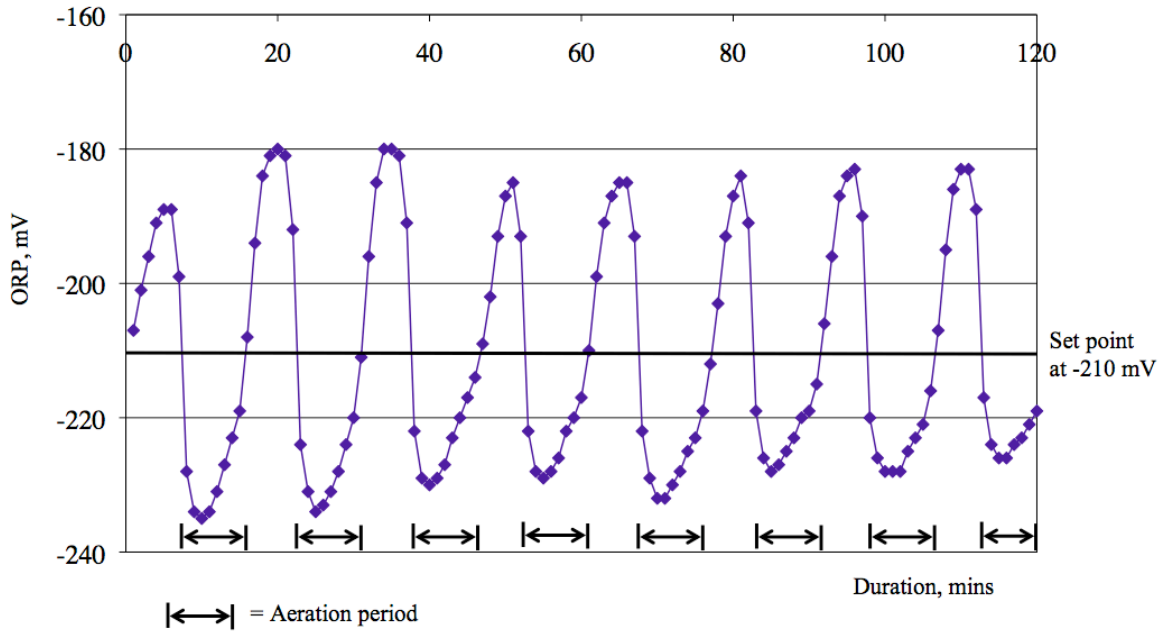

Figure 3 – ORP profile of the SOU.

Figure 3 demonstrates 8 cycles of the ORP profile of the SOU during a 2-hour period at the -210 mV set point. Before the -210 mV set point was reached, the aeration rate was approximately at 7.0 ml/min (continuous aeration). During the -210 mV set point, average aeration rate decreased to 3.1 ml/min due to intermittent aeration, corresponding to an O_2 concentration of 0.31% during continuous aeration and 0.16% during intermittent aeration. Since ORP is inversely proportional to logarithmic sulfide concentration (Janssen *et al*., 1998), the cycling pattern of ORP was likely to be the result of fluctuations of sulfide concentration in the SOU. It is interesting to note that the off-gas H_2S concentration during the period with or without aeration stayed less than 1 ppm. This means that only slight changes of dissolved sulfide concentrations could change the ORP and allow aeration to start/stop, adjusting the amount of air injected into the SOU.

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Optimizing aeration rate by ORP. Optimization was conducted by varying the ORP set point to yield the minimum aeration required for hydrogen sulfide removal in biogas. The set points were randomly set in the following sequences to be -360 mV for 2 days, -410 mV for 1 day, -460 mV for 3 days, -470 mV for 2 days, -460 mV for 4 days, -410 mV for 1 day, -435 mV for 1 day, -420 mV for 1 day, -410 mV for 1 day, -390 mV for 1 day, and then -370 mV for 1 day. The ORP set points, the measured ORPs, and hydrogen sulfide concentrations at SOU headspace with the corresponding aeration rates were plotted from low to high in Figure 4.

From Figure 4, the ORP of the SOU followed well with the ORP set point. Increases in aeration rates directly resulted in the reduction in hydrogen sulfide at the SOU. For ORP set points higher that -460 mV, increased ORP set point resulted in increased aeration rates. However, at ORP set points of -460 mV or less, increases in aeration rates did not affect the ORP. It is suggested that the ORP set point and the aeration rate needs to be more than -460 mV and 2.0 ml/min to successfully remove hydrogen sulfide from biogas by using the integrated system.

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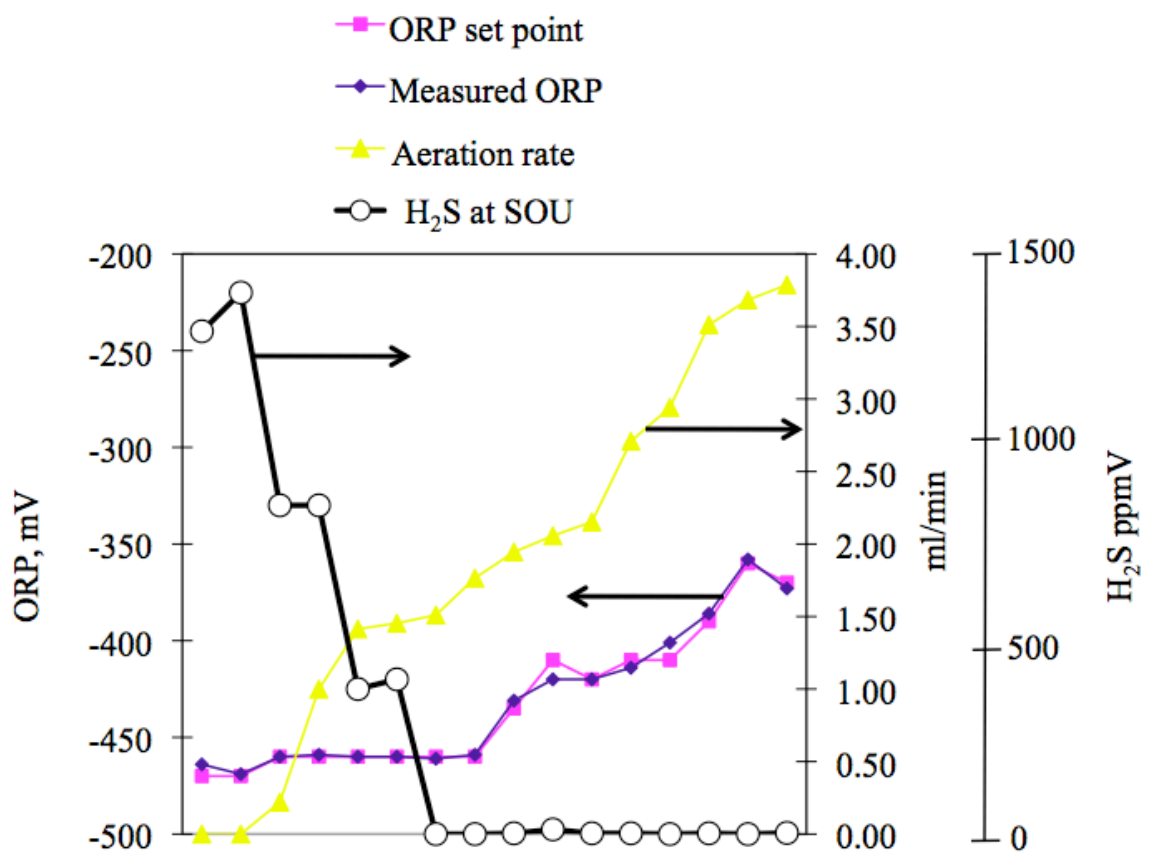

Figure 4 – The relationship of ORP, aeration rate, and hydrogen sulfide at the SOU.

Long-term experiments: During long-term operation, a continuous aeration method was used to remove hydrogen sulfide from the biogas. The goal was to find the minimum aeration rate that resulted in the lowest hydrogen sulfide concentration in the biogas at the SOU. ORP changes were monitored throughout the study. The aeration rates were varied between 2.0 to 6.0 ml/min during two months of the experiment. It was found that aeration rates needed to be approximately 4.0-5.0 ml/min to ensure that the hydrogen sulfide in the biogas at SOU was less than 5 ppmV. This aeration rate was more than the 2.0 ml/min suggested earlier. One of the reasons for this is that elemental sulfur formed in the SOU could possibly be reduced to

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hydrogen sulfide with the biodegradable COD present, adding extra sulfide load to the SOU. Therefore, the SOU required more air. Even at this high range of aeration rates, the ORP at the SOU was approximately -450 mV.

Comparison experiments: The comparison experiments between before and during micro-aeration were conduced at different periods of time, approximately six months apart. However, the system was operated in the same manner. The biogas production, the percentage of methane, and the VFA in the reactor were approximately the same before the beginning of the micro-aeration experiment. Air injection of 5 ml/min was chosen to be the target continuous aeration rate. During the two experiment periods, all necessary tests were conducted for 7 days in a row. Table 2 shows the performance of the integrated system before and during micro-aeration from one experiment. The results demonstrate that while the biogas production rates of the two periods were different, the methane production rates were comparable. During micro-aeration, the hydrogen sulfide concentrations in the head space of SOU were never more than 4 ppmV and, most of the time, were less than a detection limit of 1 ppmV. The percentage of methane in the biogas was slightly reduced as a result of N_2 and O_2 addition during micro-aeration. The ORP levels of the digester and SOU increased from -477 and -461 mV to -465 and -446 mV, respectively. Dissolved sulfides in the effluents from the digester and SOU decreased by approximately 80%. During micro-aeration, it was estimated that more than 98% of the sulfide in gas and liquid phases was converted to elemental sulfur, which resulted in a sulfide removal rate of 0.24 kg-S/m^3-SOU/day. As mentioned before, in theory, the molar oxygen/sulfide consumption (O_2/S^{2-}) of the biological sulfide oxidation to elemental sulfur needs to be at 0.5. However, in this pilot-scale experiment, the oxygen consumption rate was 1.36 kg-O_2/m^3-

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SOU/day, which resulted in the O_2/S^{2-} of 5.6. In both conditions, COD and SCOD reductions of the integrated system were approximately 80 and 90%, respectively. However, the SCOD of the SOU at influent and effluent was slightly reduced from 570 to 440 mg/L. VFA and alkalinity ratios were less than 0.03 in both cases, indicating that the integrated system was healthy and not inhibited by the addition of small amount of air.

Table 2 – Comparison between the performance of the system with and without micro-aeration.

	Before aeration		After aeration	
	Reactor	SOU	Reactor	SOU
Biogas				
N_2, %	0.5 ± 0.1[1]	NT	5.8 ± 0.8	6.8 ± 1.0
CH_4, %	65.6 ± 0.6	NT	63.3 ± 2.2	62.6 ± 2.4
CO_2, %	33.6 ± 1.1	NT	30.2 ± 1.3	29.8 ± 1.1
O_2, %	NT	NT	0.4 ± 0.1	0.7 ± 0.1
H_2S, ppmV	2450 ± 150	2420 ± 170	29.0 ± 5.8	1.7 ± 1.7
Biogas producition, L/d	54.2 ± 4.5		59.8 ± 2.6	
Methane production, L/d	35.0 ± 0.6		37.8 ± 0.1	
Liquid				
Sulfide, mg/L	17.7 ± 1.7	17.4 ± 1.7	1.1 ± 1.1	ND
Sulfate, mg/L	ND	ND	0.1 ± 0.2	12.5 ± 8.3
Thiosulfate, mg/L	ND	ND	ND	ND

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ORP, mV	-477 ± 8	-461 ± 7	-465 ± 12	-446 ± 3
pH	7.17 ± 0.01	7.20 ± 0.01	7.24 ± 0.03	7.23 ± 0.01

[1]Standard deviation of seven data points

NT = Not tested

ND = Not detected

Batch experiment

Methanogenic/sulfidogenic activities and specific oxygen uptake rates were studied using biomass from two different periods—with and without micro-aeration. The activity tests were to evaluate the performance of the different groups of biomass in both the digester and the SOU. Table 3 summarizes the results obtained from the batch experiments. The results showed no change in methanogenic activities utilizing different substrates. This confirms the results from the continuous experiments that demonstrated the methane production rates from the two conditions were similar. Even though oxygen is considered toxic to methanogens, the amount of oxygen injected into the system was not high enough to cause a toxicity effect. However, after air injection, the activities of sulfate reducing bacteria were increased, especially, the sulfate reducing bacteria using hydrogen as substrate—the activities were more than doubled when oxygen was present in small amounts. Specific oxygen uptake rates of the biomass in the digester at different conditions were similar; however, those of the biomass in the SOU were significantly different. The uptake rate of the biomass in the SOU was almost tripled, indicating that aerobic or facultative bacteria were active when oxygen was present.

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Table 3 – The results of biomass activity test.

	Before aeration		After aeration	
	Reactor	SOU	Reactor	SOU
Methanogenic activities				
g-CH_4-COD/g-VS-day				
Acetate	0.21 ± 0.02	0.18 ± 0.01	0.25 ± 0.01	0.25 ± 0.01
Glucose	0.19 ± 0.02	0.16 ± 0.01	0.17 ± 0.01	0.15 ± 0.01
Hydrogen	0.49 ± 0.18	0.47 ± 0.01	0.48 ± 0.02	0.46 ± 0.10
Sulfidogenic activities				
mg-SO_4-COD/g-VS-day				
Acetate	6.30 ± 0.54	5.99 ± 0.72	7.15 ± 0.41	6.76 ± 0.28
Glucose	30.05 ± 2.21	29.35 ± 2.16	31.59 ± 7.75	35.13 ± 1.13
Hydrogen	44.13 ± 8.93	44.28 ± 7.93	104.73 ± 12.03	128.26 ± 31.36
Specific oxygen Uptake rates				
mg-O_2/g-VS-hr				
Glucose	3.90 ± 0.07	2.67 ± 0.09	3.80 ± 0.15	7.52 ± 0.15

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CONCLUSIONS

It was possible to use the integrated system to remove hydrogen sulfide from biogas (1-2 ppmV) with elemental conversion of more than 98% and minimal sulfate production. The activities of the different groups of methanogens were not changed after micro-aeration, confirming the results that there was no deterioration of methane production rates in the continuous experiment. When small amounts of oxygen were present, hydrogenotrophic sulfate reducing, aerobic, and/or facultative bacteria became significantly more active than the condition without oxygen. The findings of this study are significant in providing a preliminary design for an integrated sulfide removal system that is efficient, robust and yet inexpensive.

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MICRO-AERATION FOR HYDROGEN SULFIDE REMOVAL FROM BIOGAS

A paper to be submitted to *Water Research*

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ABSTRACT

Biogas utilization for electricity generation and other purposes can be hindered by the present of hydrogen sulfide because of its corrosive property to metals and production of sulfur dioxide after combustion. In this research, ORP-controlled micro-aeration technique was proposed to remove hydrogen sulfide from biogas. A 3-feet tall sulfide oxidizing unit (SOU) was equipped with a diffuser at the bottom for the dispersion of sulfide-laden biogas and injected air throughout the column. Hydrogen sulfide in biogas dissolved into a medium, i.e. the effluent of an anaerobic digester, and reacted with oxygen in air, resulting in sulfide-free biogas (< 1 ppmV) with minimal oxygen (< 1%) in the off-gas. A long-term testing revealed that a ORP set point of -200 mV could be used as a controlling parameter for micro-aeration if the pH of medium was more than 6. A short-term testing was conducted to estimate the maximum sulfide removal rate at different aeration and biogas recirculation rates. It was found that the maximum sulfide removal rate of 0.61 kg/m^3-day could be obtained when the SOU was operated at biogas

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recirculation rate of 0.4 L/min (22.86 m^3/m^3-hr) and airflow rate of 1.0 ml/min (0.06 m^3/m^3-hr). Additional experiment also revealed that the ORP controlled aeration was sensitive enough to prevent oxygen overdosing (dampening effect) during unexpected surges of aeration.

KEYWORDS

Hydrogen sulfide removal, anaerobic digester, biogas, ORP, micro-aeration, control

INTRODUCTION

Anaerobic treatment of waste streams containing sulfate/protein contributes several different types of sulfur-containing compounds, including hydrogen sulfide, mercaptan, etc., in biogas. The sulfur-containing compounds are not only malodorous and harmful but also hinder the use of biogas as renewable energy source, such as the uses in boiler for heating, internal combustion engine for electricity production, and other catalytic processes (Brown, 2003).

When wastes containing sulfur compounds are fed to the digester, sulfate reducing bacteria (SRB), will reduce sulfur containing compounds to sulfides (Clanton and Schmidt, 2000), resulting in biogas contaminated with hydrogen sulfide. The hydrogen sulfide in biogas limits the usage of biogas in many down stream processes. The most popular use of biogas is the electricity generation via internal combustion engine. However, many engine manufactures limit the hydrogen sulfide in biogas to be less than 100 ppmV (Zacari, 2003). To inject methane generated from digester to pipeline, hydrogen sulfide concentration is needed to be less than 4

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ppmV (Amirfakhri et al., 2006; Sublette and Sylvester, 1987a). In addition, burning of biogas containing hydrogen sulfide would produce sulfur oxides, which is a main precursor of acid rain that can damage any living organism and structure.

Hydrogen sulfide can be removed from biogas by chemical (Droste, 1997; Kohl and Neilsen, 1997), physiochemical (Guo *et al*., 2007), and biological processes (Jensen and Webb, 1995. Among these processes, biological sulfide removal is considered to be the cheapest alternative (Syed *et al*., 2006;) due to high capital and operating costs and labor intensive nature of the counterparts (Buisman *et al.,* 1991).

In biological sulfide removal from gas or liquid streams, elemental sulfur is a preferred as a final product due to the lesser amount of oxygen requirement than having sulfate as end product (Janssen *et al.*, 1997 and 1998). Since element sulfur is insoluble, it can be removed from the streams relatively easy, which results in the reduction of overall sulfur species. In theory, elemental sulfur would be the only product if the molar ratio of oxygen/sulfide consumption (O_2/S^{2-}) is 0.5. However, the maximum elemental sulfur formation occurred at O_2/S^{2-} of 0.6 to 1.0 (Janssen *et al*., 1995).

During the sulfur formation, dissolved oxygen was never exceed 0.1 mg/L, giving the difficulty in controlling the oxygen input to the sulfide removal reactor. Janssen *et al.*, 1998 introduced the use of oxidation-reduction potential (ORP) to control O_2/S^{2-}. By controlling ORP at -137 mV, elemental sulfur was found to be a major product, accounted for over 80% of total sulfide loaded. However, Krishnakumar *et al.* (2005) used similar reactor set up to find optimal ORP to

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maximize elemental sulfur production and found that ORP range of -400 to -300 mV contributed around 80% sulfur recovery when the reactor was loaded by 19 kg-S^{2-}/m^3-day. Khanal and Huang, 2003 used ORP to control oxygen injection to an upflow anaerobic filter, suffered from high level of sulfate (6000 mg/L) in the influent. By setting operating ORP at 25 mV above operating ORP, the methane generation of the reactor improved by 46%. To remove small amount of hydrogen sulfide in biogas, small amount of air can be injected into anaerobic digester at a rate of 7.5 % of biogas production, which can reduce hydrogen sulfide from about 680 to less than 10 ppmV (Ikbal *et al*., 2003).

In this research, we proposed a low-cost, robust sulfide removal technique to removal sulfide from biogas generated from an anaerobic digester treating high solid wastes. Because sulfide oxidizing unit (SOU) was not filled with packing media, the SOU was able to cope with much high solids than other sulfur oxidizing columns (Krishnakumar *et al*., 2005, Khanal *et al.*, 2003, Koe and Fang, 2000). Since, the SOU did not require nutrient, trace element addition, nor pH adjustment, it offer considerable advantages over typical biological sulfide removal systems.

For full scale reactor design, the objectives of this research were (1) to estimate the maximum sulfide removal rates when a sulfide oxidation unit (SOU) was operated at various biogas recirculation rate and air injection rate and (2) to examine the feasibility of using ORP based micro-aeration technique for long-term hydrogen sulfide removal from biogas for maximizing elemental sulfur formation with minimal sulfate and thiosulfate formation. In addition, the mass balance of sulfur species (including sulfate, thiosulfate, sulfide, and elemental sulfur) was conducted.

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METHODOLOGY

The sulfide oxidizing unit

Figure 1 shows a hydrogen sulfide removal system. The system consisted of a one-liter sulfide oxidizing unit (SOU) connected to an pilot scale anaerobic digester, a continuous stirred tank reactor (CSTR) with an internal settling zone, that had working volume of 92 L. The 1.5-inch ID SOU was operated with liquid height of approximately 3 feet. The effluent from the digester was occasionally pumped into the SOU to provide medium for sulfide removal.

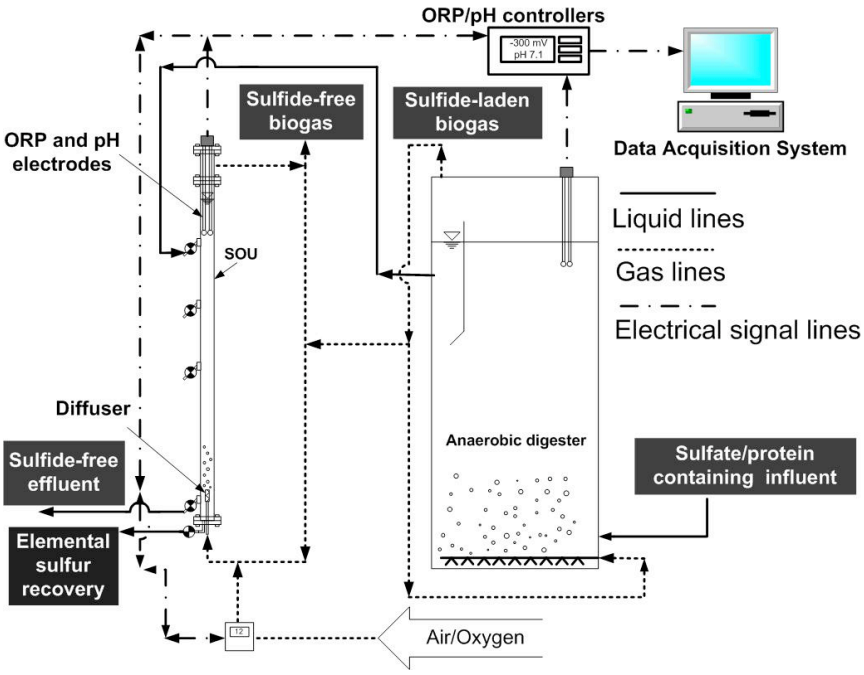

Figure 1 – Schematic of the sulfide removing system.

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Sulfide-laden biogas produced in the digester was mixed with small amount of air before being forced through a fine diffuser located at the bottom of the SOU. In the SOU, hydrogen sulfide in the biogas dissolved into the medium and reacted with oxygen in the injected air to form elemental sulfur. After passing through a foam trap (not shown), sulfide-free biogas exited the system. Hydraulic retention times (HRTs) of the pilot scale digester was controlled at 20 days. The digester was continuously mixed by means of biogas recirculation at the rate of 1.5 L/min (0.016 L/$L_{digester}$-min) whereas the biogas recirculation rate of the SOU was set to either 0.2 or 0.4 L/min (0.2 or 0.4 L/L_{sou}-min). Both the SOU and the anaerobic digester were operated at a room temperature of 25±2°C. The liquid and the head space volumes of SOU were 1.05 and 11.1 L, respectively.

Initially, the digester was inoculated with anaerobic digester sludge from a local wastewater treatment plant and fed with a synthetic organic substrate. Fifteen liters of the synthetic organic substrate consist of 338.1 g of commercial dog food (with minimum 27% of crude protein, minimum of 15% crude fat , maximum of 4% crude fiber, maximum 4% of moisture by weight), 50 g of $NaHCO_3$, and 15 ml of trace element solution (prepared by adding 10 g of $FeCl_2.4H_2O$, 2.0 g of $CoCl_2.6H_2O$, 1.0 g of EDTA, 500 mg of $MnCl_2.4H_2O$, 200 mg of Resazurin, 142 mg of $NiCl_2.6H_2O$, 123 mg of Na_2SeO_3, 90 mg of $AlCl_3.6H_2O$, 50 mg of H_3BO_3, 50 mg of $ZnCl_2$, 50 mg of $(NH_4)_6MoO_{24}.4H_2O$, 38 mg of $CuCl_2.2H_2O$, and 1.0 ml of HCl (37.7% solution) into distilled water to make 1 liter). Substrate preparation was conducted by soaking of dog food for 1 day, adding $NaHCO_3$ and trace element solution, and adjusting the volume to 15 L by tap water. The substrate was kept in a 4°C refrigerator prior to feeding. The organic and COD

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loading rate to the digester were approximately 0.8 g-VS/L-day and 1.2 g-COD/L-day, respectively. Prior to the experiments, the anaerobic digester had been operated for more than a year to ensure the steady state condition was reached. Table 1 shows chemical analysis of the effluent and biogas compositions from the anaerobic digester.

Table 1 – The chemical analysis of the effluent and biogas compositions.

Parameters	
Chemical analysis	
TS, g/L	5.0±0.5[a]
VS, g/L	1.7±0.4
TSS, g/L	1.0±0.3
VSS, g/L	0.9±0.2
Alkalinity, g/L as $CaCO_3$	4.8±0.2
pH	7.24±0.03
TCOD, g/L	3.2±0.3
SCOD, g/L	0.6±0.1
SO_4, mg/L	ND
Volatile fatty acids (VFA), mg/L as acetic acid	61±23
Sulfides, mg/L	22.6±2.6
$S_2O_3^{2-}$, mg/L	ND
Biogas characteristics	
Biogas production rate, L/day	57.2±5.3

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CH_4, %	65.8±1.9
CO_2, %	33.6±1.5
N_2, %	0.2±0.1
O_2, %	ND
H_2S, ppmV	2170±80

[a]An average and standard deviation of more than 5 data points

ND = Not detected

Aeration control. Two set of pH and ORP probes were installed on top of the digester and SOU. Air was supplied by compressed air tank equipped with a regulator to control airflow rate. Every minute, the ORP/pH controller would receive signal from the ORP and pH electrodes located at the SOU. During the period when aeration was controlled by ORP, the ORP/pH controller would send signal to a set of solenoid valves to OPEN (injecting air) or CLOSE (stop injecting air), depending on ORP set point and ORP level at the moment. However, during the period when constant aeration was utilized, the set of solenoid valves would be OPEN all the time to allow air into the SOU. Airflow rate into the SOU was monitored with a digital flow meter that connected to a computer. The computer was used as a data acquisition and monitoring system so that instantaneous and average airflow rates could be calculated. To prevent pressurization of air line that could result in a surge of airflow into the SOU during the beginning of aeration, two solenoid valves (one normally OPEN and the other normally CLOSE) were installed. This installation would allow air to exit the system during non-aeration period and allow air at predetermined flow rate into the SOU during aeration period.

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Short-term experiment

The estimation of maximum sulfide removal rate. In normal operation, the sulfide removal rate of the SOU is only as high as the sulfide loading rate to the SOU. The maximum sulfide removal rate can only be estimated when biogas containing sulfide is injected at the rate at which the sulfide loading rate is higher than the its removal rate, i.e. when the breakthrough of hydrogen sulfide occurs. Because of the limited biogas supply of the pilot-scale anaerobic digester to the SOU, the sulfide removal rate is always underestimated. However, during initial reduction of sulfide after air injection, the sulfide is reduced at the rate higher than the sulfide loading rate since biogas containing hydrogen sulfide is continuously injected to the SOU, yet hydrogen sulfide in the off-gas is reduced to less than 1 ppmV in merely hours. Therefore, utilizing a mass balance technique, the maximum sulfide removal, which is higher than sulfide loading rate, can be estimated.

This experiment consisted of six tests, each operated at different biogas recirculation rate (0.2 and 0.4 L/min) and airflow rate (0.2, 0.4, and 1.0 ml/min). To estimate the maximum sulfide removal rate, both medium and gas were sampled hourly from before air injection to when the hydrogen sulfide in the off-gas was reduced to less than 10 ppmV. Then, a mass balance equation was applied to the data obtained from different intervals. With at least two-hour duration, the interval that yielded the highest sulfide removal rate was chosen as the sulfide removal rate for the test. Before each test, the SOU was cleaned and filled with new batch of medium from the anaerobic digester.

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From a simple mass balance equation,

$$IN - OUT - Accumulation = \mathrm{Re}action$$

Given,

$$IN - OUT = Q_{in}C_{S,in} - Q_{out}C_{S,out}$$

$$\mathrm{Re}action = r_S V$$

$$Accumulation = \frac{dn_S}{dt} = Accu_{gas} + Accu_{liquid}$$

$$Accu_{gas} = \frac{dn_{S,g}}{dt}$$

$$Accu_{liquid} = \frac{dn_{S,l}}{dt}$$

$$dn_{S,g} = n_{S,g,1} - n_{S,g,0}$$

$$dn_{S,l} = n_{S,l,1} - n_{S,l,0} + \sum n_{S,l,add,i} - \sum n_{S,l,remove,i}$$

$$dt = t_1 - t_0$$

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$$n_{S,g,0} = C_{S,g,0} V_h$$

$$n_{S,l,0} = C_{S,l,0} V$$

$$n_{S,g,1} = C_{S,g,1} V_h$$

$$n_{S,l,1} = C_{S,g,1} V$$

$$\sum n_{S,l,add,i} = \sum C_{S,l,add,i} V_{add,i}$$

$$\sum n_{S,l,remove,i} = \sum C_{S,l,remove,i} V_{remove,i}$$

Therefore, the mass balance becomes

$$r_S = \frac{Q_{in} C_{S,in} - Q_{out} C_{S,out} - (C_{S,g,1} - C_{Sg,0}) \frac{V_h}{dt} - (C_{S,l,1} - C_{S,l,0}) \frac{V}{dt} - \sum C_{S,l,add,i} \frac{V_{add,i}}{dt} + \sum C_{S,l,remove,i} \frac{V_{remove,i}}{dt}}{V}$$

where Q_{in} and Q_{out}= Inflow and Outflow biogas rate (L/hr) from time t_0 to t_1, $C_{S,in}$ and $C_{S,out}$= Average inflow and Outflow hydrogen sulfide concentration in gas phase (mole-S/L-gas) from time t_0 to t_1, $C_{S,g,0}$ and $C_{S,g,1}$= Hydrogen sulfide concentration in gas phase (mole-S/L-gas) at time t_0 and t_1, $C_{S,l,0}$ and $C_{S,g,1}$= Sulfide concentration in liquid phase (mole-S/L) at time t_0 and t_1, r_S= reaction rate (mole/L-hr or mg/L-hr), $n_{S,g,0}$ and $n_{S,g,1}$= mole of hydrogen sulfide in gas

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phase at time t_0 and t_1, $n_{S,l,0}$and $n_{S,l,1}$ = mole of sulfide in liquid phase at time t_0 and t_1, $n_{S,l,add,i}$and $n_{S,l,remove,i}$= mole of sulfide in liquid phase of the medium added /removed due to ith sampling between t_0 and t_1, $C_{S,l,add,i}$and $C_{S,l,remove,i}$= Sulfide concentration in liquid phase (mole-S/L) of the medium added /removed due to ith sampling between t_0 and t_1 at, V_h = the head space volume of the SOU (L), V = liquid volume of the SOU (L), $V_{add,i}$and $V_{remove,i}$ = volume of the medium added /removed due to ith sampling between t_0 and t_1, and t = time (hr). Since, the liquid height of the SOU was maintained constant, $\sum V_{add,i} = \sum V_{remove,i}$.

ORP-controlled aeration rate. In this experiment, the effect of instantaneous air injection rate on average aeration rate was studied. The air injection of controlled by ORP. Whenever the ORP of the SOU was below -200 mV for 5 seconds, air injection would start at predetermined instantaneous air injection rates (approximately 1.3, 1.7, 2.5, 4.8, and 12.9 ml/min) and, after the ORP increase more than -200 mV for 5 seconds, the air injection would stop. The on-and-off cycle repeated. To calculate the average aeration rate, the total amount of air injected during five cycles (five air injections) was divided by the total time taken to complete the five cycles. On the other hand, the instantaneous air injection rate was defined as the amount of air injected during air injection periods divided by air injection time. To minimize the effect of pH change on ORP, the experiment was conducted with a very narrow pH range of 7.10 to 7.15. Biogas injected to the SOU in the testing period was consistent in terms of the concentration of each constituent, especially hydrogen sulfide, and the amount the biogas. The biogas recirculation rate at the SOU was 0.4 L/min.

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Long-term experiment

The long-term experiment was conduced to mimic the operation of the SOU and to examine the feasibility of using the ORP as a controlling parameter for sulfide removal. In the real reactor operation, the medium would be replaced to maintain the operating pH of the SOU. However, to simulate the worse case scenario of the reactor operation, the pH of the SOU was not controlled and allowed to deplete as sulfuric acid formed. In this experiment, the aeration was controlled by ORP for approximately two-third of the experiment that lasted about 30 days. The ORP was set to inject air when the ORP went below -200 and 0 mV for more the 5 seconds. Prior to the experiment the SOU was cleaned and filled with new medium from the anaerobic digester. The SOU was operated at biogas recirculation rate of 0.4 L/min and airflow rate of 1.0 ml/min. The ORP and pH values reported herein were averages of daily data.

Analytical methods

Methane, carbon dioxide, and nitrogen in the biogas were analyzed by a Gow Mac series 350 GC-TCD fitted with a 84-mm (3.3-in.) stainless-steel column packed with Porapak T (60/80 mesh) (GOW-MAC Instrument Company, Bethlehem, PA, USA). Helium was used as the carrier gas at a flowrate of 35 mL/min. The temperatures of the injection port, oven, and detector were at 150, 50, and 100°C, respectively. Oxygen and hydrogen sulfide in the biogas were analyzed with a Gow Mac series 400 GC-TCD fitted with Chromosil ‘310 and Molesieve 18 80/100 (8 ft) column. Helium was used as the carrier gas at flow rate of 30 ml/min. The temperatures of the injection port, oven, and detector were at 100, 60, and 115°C, respectively. Hydrogen sulfide

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was also measured by BW defender multi-gas detector (D4-2002, BW Technologies, Arlington, TX, USA) and colorimetric gas detection tubes (RAE systems, San Jose, CA, USA). All gas production data reported were standardized to standard temperature (0°C) and pressure (760 mm Hg). Sulfate and thiosulfate were analyzed by ion chromatograph (Dionex model DX 500, Dionex Cooperation, Sunnyvale, CA, USA) with AN1 anionic column (Varian Inc., Palo alto, CA, USA), and ASRS® ULTRA II, 4 mm, suppressor (Dionex P/N 061561) at 50 mA suppressor conductivity. Sodium carbonate/biocarbonate eluent (1.8/1.7 mmole/L) was used as mobile phase at a flow rate of 1 ml/min. Elemental sulfur was estimated using mass balance approach (Krishanakumar *et al*., 2005). pH and ORP was monitored through pH/ORP controller (Consort R305, Consort nv, Belgium). Airflow rate was monitored by digital differential pressure air flow meter with RS-232 (EW-32446 series, Cole-Parmer, Vernon Hills, IL, USA). The pH/ORP controller and digital gas flow meter were connected to a personal computer for data requisition. Volatile fatty acids (VFAs), Total solids (TS), Volatile solids (VS), Total suspended solids (TSS), Volatile suspended solids (VSS), aqueous sulfide, alkalinity, and COD measurements were made in accordance with the procedures listed in Standard Methods (APHA *et al*., 1995). The soluble COD (SCOD) was defined as the COD component that passed through a 0.45-μm pore size filter. All equipment was calibrated before every experiment.

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RESULTS AND DISCUSSION

Short-term experiment

The estimation of maximum sulfide removal rate. In this experiment, the SOU was subjected to different airflow (0.2, 0.4, and 1.0 ml/min) and biogas recirculation rates (0.2 and 0.4 L/min). Figure 2 shows the reduction of hydrogen sulfide in the off-gas of the SOU. It can be seen that the maximum sulfide removal rate occurred during the first two to three hours after air injection. It took approximately 6.5, 5.0, and 3.0 hours for hydrogen sulfide concentration in the off-gas of the SOU to be reduced to less than 10 ppmV for the SOU with airflow rate of 0.2,0.4, and 1.0 ml/min, respectively. However, after 1 days of aeration, the concentration could be reduced to less than 1 ppmV at all operating conditions.

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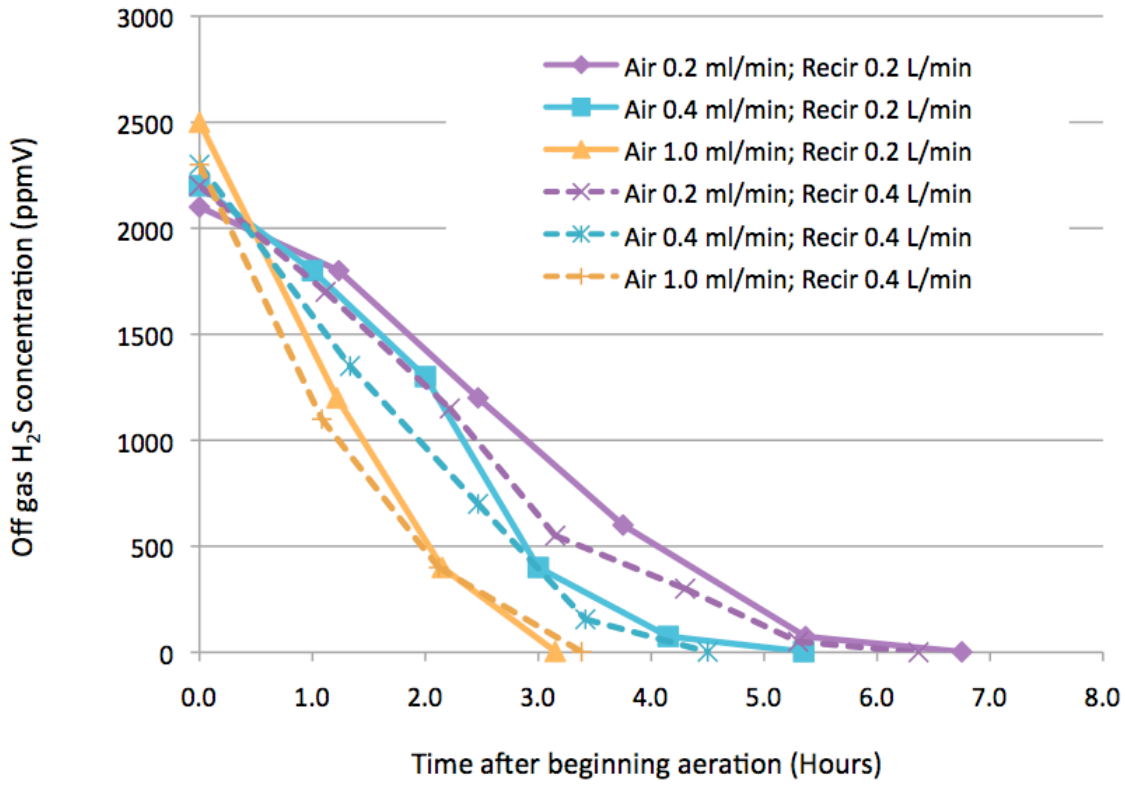

Figure 2 – Reduction of hydrogen sulfide in the off-gas of the SOU.

After unit conversion, the resulting terms in the above mass balance equation are shown in Table 2. Approximately 50% of sulfide removal was contributed from the reduction of hydrogen sulfide in the headspace due to large headspace volume of the SOU (11.1 L). From Table 2, it can be seen that increases in airflow and/or biogas recirculation rates increased the reaction rate, which responded to increases in the changes of ORP and O_2 content in the headspace of the SOU. The experiment revealed that sulfide removal rate was significantly affected by the change of airflow rate. When the airflow rate increased two-fold from 0.2 to 0.4 ml/min, the sulfide removal rate increased by approximately 31 and 27% at biogas recirculation rate of 0.2 and 0.4 L/min, respectively. However, with the same airflow rate, double the biogas

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recirculation rate only slightly improved sulfide removal rate (approximately 10% or less). The highest sulfide removal rate of 25.2 mg-S/hr or 0.61 kg-S/m^3-day was obtained from the SOU subjected to airflow and biogas recirculation rate of 1.0 ml/min and 0.4 L/min, respectively. This suggests that it may not be wise to increase biogas recirculation rate since it would likely just increase operation cost without a major gain in sulfide removal rate. This experiment also demonstrated that sulfide removal at the rate higher than the sulfide loading rate (in this case, 8.1 mg-S/L-hr or 0.19 kg/m^3-day) could be estimated by using the previously mentioned mass balance equations.

Table 2 – The performance of the SOU.

Airflow rate	Biogas recirculation rate	IN-OUT	$Accu_{gas}$	$Accu_{liquid}$	Reaction ($r_S V$)	Change in ORP	Change in O2
ml/min	L/min	mg-S/hr	mg-S/hr	mg-S/hr	mg-S/hr	mV/hr	%/hr
0.2	0.2	3.0	-6.7	-3.5	12.6	5	0.03
0.4	0.2	4.2	-8.5	-4.6	16.5	9	0.06
1.0	0.2	2.5	-13.8	-9.2	24.3	19	0.12
0.2	0.4	3.0	-7.4	-4.2	13.9	7	0.04
0.4	0.4	3.6	-8.9	-6.1	17.7	24	0.06
1.0	0.4	2.4	-15.7	-8.5	25.2	46	0.14

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ORP-controlled aeration rate. In this experiment, ORP was used as a controlling parameter for aeration control. Before the experiment, the SOU was operated at a constant airflow and biogas recirculation rates of 1.0 ml/min and 0.4 L/min, respectively. The hydrogen sulfide concentration was maintained at less than 1 ppmV before and throughout the experiment. Figure 3 shows the effect of instantaneous airflow rate on ORP and average airflow rate. Five waves represented five ORP profiles obtained from five tests that varied instantaneous airflow rates—1.3, 1.7, 2.5, 4.8, and 12.9 ml/min from left to right. There are five cycle in each wave. Each cycle consisted of one air injection, which was responded to the change of ORP at the moment. Whenever the ORP stayed below the set point of -200 mV for 5 seconds, the air injection started. From the figure, it can be seen that when the instantaneous airflow rate increased, each ORP cycle was higher in amplitude and wider, taking longer time to finish five cycles. The differences between maximum and minimum ORP and the durations of air injection for instantaneous airflow rates of 1.3, 1.7, 2.5, 4.8, and 12.9 ml/min were summarized in Table 3.

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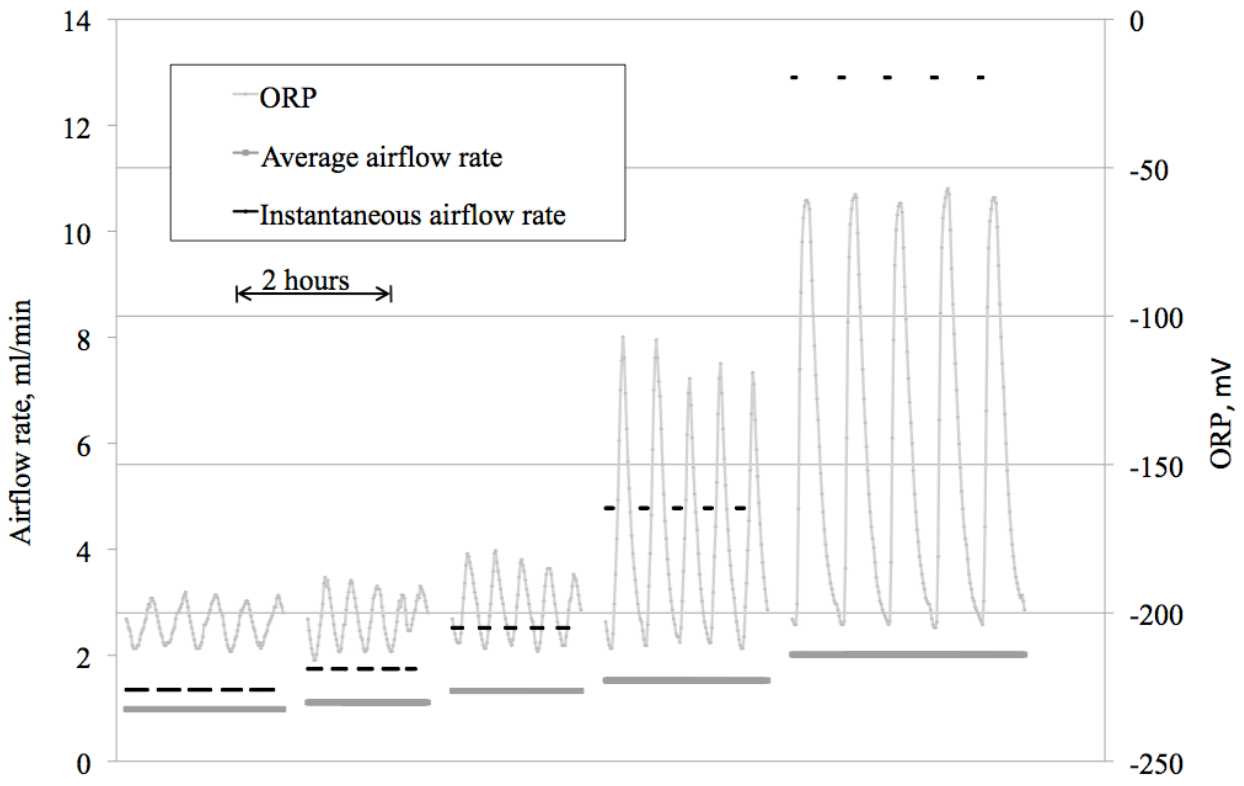

Figure 3 – ORP profiles responded from different air injection rates.

In response to the increase in the instantaneous airflow rates, the ORP raised quickly and stopped airflow to the SOU. After oxygen was depleted, the ORP went down again. The higher the instantaneous airflow, the higher the ORP went up, which took longer time for it to come down. This limited the amount of air injected to the SOU by acting like dumpener for air injection. If it had not been for ORP controlled aeation technique, the percentage of air injection would have been 23 %, and the oxygen content in biogas would have been 5 % for the highest air. Instead, the average airflow rate was only 2.0 ml/min, 6.5 times less than the instantaneous airflow rate, and the oxygen content in biogas was approximately 1.0%. This indicates that the

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ORP controlled aeration was sensitive enough to prevent oxygen overdosing. Moreover, the ORP control technique can be used as safety measure for preventing too much air from being injected and causes combustion failure at biogas engine.

Table 3 – Effect of the different instantaneous airflow rate on ORP profiles and characteristics of air injection.

Parameters					
Instantaneous airflow, ml/min	1.3	1.7	2.5	4.8	12.9
Differences between maximum and minimum ORP, mV	20	28	34	105	148
Duration of air injection, min	18	11.4	9.6	7.0	4.6
Average airflow rate, ml/min	1.0	1.1	1.3	1.5	2.0

Long-term experiment

In long-term experiment, the SOU was subjected to aeration with ORP controlled technique. The experiment consisted of two phases whereby the aeration was controlled by ORP and followed by constant aeration. To observe the limit of the aeration controlled by ORP, the medium of SOU was not intended to change, except for a small replacement of medium due to periodical samplings. The pH of the SOU was allowed to decrease naturally during the first 18 days of the experiment. On the day 19 and 20, the pH was gradually adjusted from

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approximately 6.4 to 5.1 by adding 6N HCl. Thereafter, the pH decreased naturally. Two ORP set points were used during the experiment to control aeration rate—the set points at -200 mV from day 1 to day 20 and at 0 mV on day 22. On day 21 and after day 22, the air injection rate was set at 1.0 ml/min with or without ORP control.

Figure 4 shows the profiles of pH, ORP, off-gas hydrogen sulfide concentration, and concentration of dissolved sulfide, sulfate, and thiosulfate during the long time experiment. In general, the removal of sulfide from biogas gradually reduced pH of the medium due to hydrogen sulfide absorption into the medium and a conversion of sulfide or other sulfur species to sulfate. The decrease of pH resulted in the increase of daily average ORP even though the ORP set point was -200 mV.

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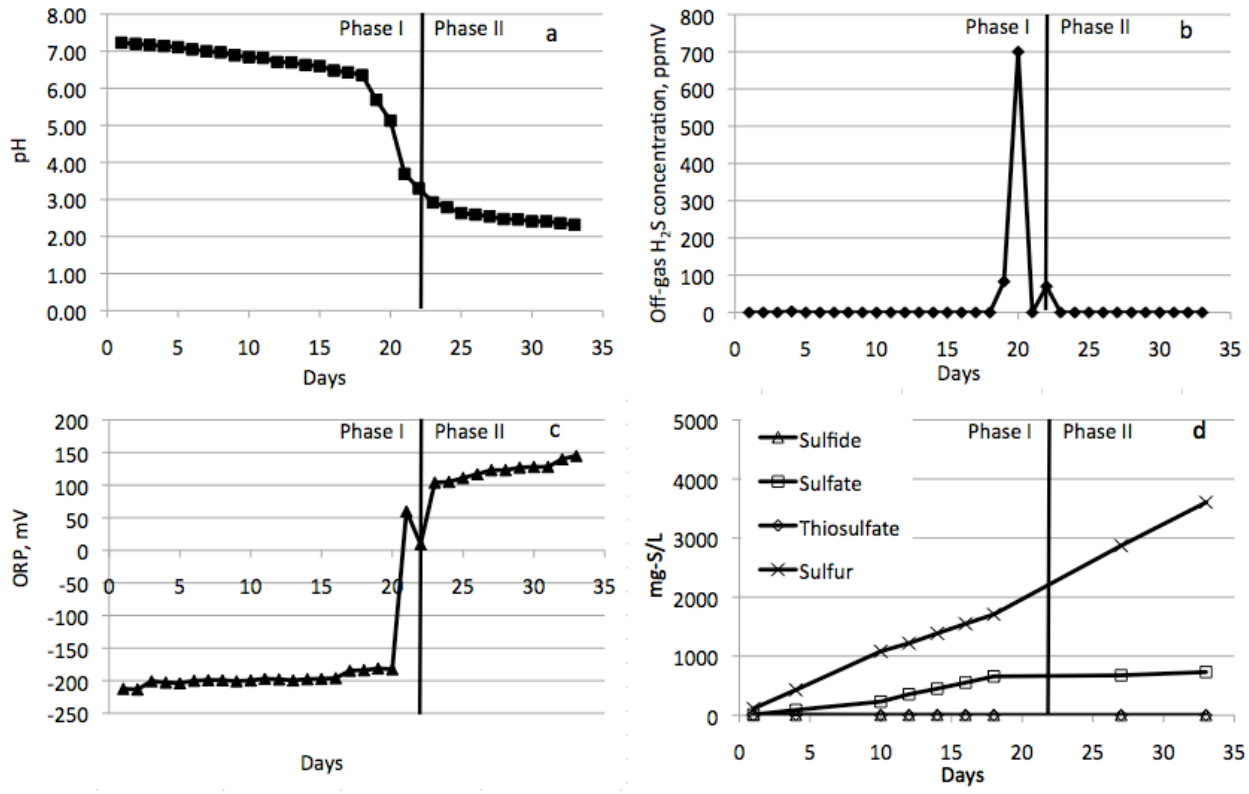

Figure 4 – The profiles of pH (a), off-gas hydrogen sulfide concentration (b), ORP (c), and concentrations of dissolved sulfide, sulfate, and thiosulfate during the long-term experiment.

Table 4 shows several characteristics of interaction between ORP and aeration. As pH decreased, average aeration rate decreased. When pH was at 7.17 on day 3, the average aeration rate was 0.54 ml/min (or 0.78 L/day). However, the rate decreased to 0.36 ml/min (or 0.52 L/day) when the pH was 6.43. This was because, regardless of the sulfide or oxygen contents in the medium, the change of pH shifted ORP value, which resulted in the deterioration of aeration control. As pH decreased, ORP value increased after each aeration but became more difficult to

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come down to the set point of -200 mV. This made the ORP waves wider and taller. During this period, the characteristics of ORP cycles also changed. The number of ORP cycles for every 100 min reduced from 4.8 to 3.5 while the difference between maximum and minimum ORP increased from 7 to 58 mV. However, the oxygen was still enough to oxidize all of sulfide in the SOU and reduce off-gas hydrogen sulfide concentration to less than 1 ppmV.

Table 4 – Effect of ORP controlled aeration on the characteristics of ORP and aeration.

Parameters							
Day	3	8	12	17	19	20	22
pH	7.17	6.97	6.71	6.43	5.69	5.12	3.30
#Cycle/100 min	4.8	4.3	3.9	3.5	2.1	0.9	1.1
Different between max and min ORP, mV	7	23	38	58	86	49	23
Air injection per cycle, min	10.8	11.6	11.0	9.0	9.5	7.0	11
Average aeration rate, ml/min	0.54	0.53	0.44	0.36	0.22	0.07	0.11

As pH was adjusted on the day 19 and 20 to 5.69 and 5.12, the average aeration rates were merely 0.22 and 0.07 ml/min, resulting in the off-gas concentration of hydrogen sulfide increased to 83 and 700 ppmV, respectively. On 21st day, the aeration was changed to continuous aeration at 1.0 ml/min, and the off-gas hydrogen sulfide concentration came down to less than 1 ppmV again. On day 22, the aeration rate was controlled by ORP with a set point of 0 mV. This improved the sulfide removal rate greatly from the set point at -200 mV, but the off-gas concentration was found to be 70 ppmV during air injection period and 128 ppmV during non-aeration period. When increasing aeration rate to 1.0 ml/min, the off-gas hydrogen sulfide

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concentration remained less than 1 ppmV even though the pH was dropped to 2.32 at the end of the experiment. At that low pH, only approximately 1 % of total sulfide can be in ionized form. On average, approximately 80% of sulfide in the biogas was converted to elemental sulfur. A maximum conversion of 85% was found after the first day of operation. However, because of sulfate production (Figure 4d), the conversion was diminished to approximately 72%. A small percentage of thiosulfate (4%) was found only the first few days of the experiment (Figure 2, phase 1), and it was not found again even at continuous aeration (Figure 2, phase II).

CONCLUSIONS

It has been demonstrated that it is feasible to control the micro-aeration by ORP for a long-term operation of hydrogen sulfide removal from biogas. However, it is required that the pH of the medium be controlled at certain range, otherwise, the ORP based aeration control will be ineffective and sulfide removal will become less efficient due to inadequate oxygen. With constant pH, ORP controlled aeration was sensitive enough to prevent oxygen overdosing, resulting in a dampening effect to maintain the average aeration rate, regardless of the change of instantaneous air injection rate. The sulfide removal rate of 0.61 kg/m^3-day was found to be maximum for a SOU with approximately 3 feet in medium height. Approximately 80% of sulfide was converted to elemental sulfur.

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MICRO-AERATION FOR SULFIDE REMOVAL AT A MUNICIPAL WASTEWATER TREATMENT PLANT

A paper to be submitted to *Water Research*

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ABSTRACT

Feasibility studies for H_2S removal from biogas by micro-aeration were conducted at the Ames Water Pollution Control Facility (AWPCF) by using different types of mediums available at the plant, i.e. plant effluent, mixed liquor, and digester supernatant. Anaerobic digesters at the plant produce approximately 60 m^3/hr of biogas (50,000 ft^3/day) with H_2S of less than 1000 ppmV. With the sulfide oxidizing unit (SOU), the goal was to remove H_2S to less than 10 ppmV with less than 2% of O_2 in off-gas. Using generalized linear regression, a model predicting output H_2S concentration, based on input H_2S concentrations, medium heights, and biogas flow rates, was suggested. With 95% confidence, output H_2S concentration was affected by changes in liquid heights the most, followed by changes in biogas flow rates. From the experiment at AWPCF, it was found that operating pHs were affected by the amount of alkalinity in the liquid media and that the removal efficiencies were affected by the operating pH. Among all the liquid

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media tested, digester supernatant showed the greatest potential with more than 99% of H_2S can be removed at operating pH of 7.0 and volumetric biogas flow rate of 21.6 m^3/m^3-hr. By increasing trace metal contents and temperature of the medium, the hydrogen sulfide removal rate was greatly improved. The operating cost of the full-scale system was estimated to be approximately $2/kg-S-removed. In addition, it was also revealed that abiotic sulfide oxidation was accounted for 95% of overall sulfide oxidation and that over 70% of H_2S was converted to elemental sulfur.

KEYWORDS

Biological sulfide removal, biogas, ORP, micro-aeration, hydrogen sulfide, municipal waste water treatment plant, model, trace metals

INTRODUCTION

In a municipal anaerobic digester, biogas often contains up to 400 mg/m^3 of siloxanes which deposits as silicon in cylinder wall and piston if engine generator is used for electricity production (Dewil *et al*., 2006). This level of siloxanes Siloxanes are often removed by absorbents e.g., activated carbon and silica gel (Schweigkofler and Niessner, 2001). Prior to siloxane removal from biogas, the removal of H_2S is a prerequisite to prevent the sulfide from blocking siloxane binding sites on the absorbents, and shortening the absorbents' life. In

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addition, the H_2S in biogas is not only poisonous but also reduces the quality of biogas to be used as a renewable energy source. The maintenance cost is expected to increase by almost 4 folds if H_2S is not reduced prior to an engine-generator set (Pipatmanomai *et al*., 2009). H_2S of less than 100 ppmV is recommended to prevent the corrosion of biogas engine (Zicari, 2003). H_2S has to be lowered to less than 4 ppmV if pipeline-grade nature gas is to be produced from digester biogas.

To minimize H_2S in biogas prior to siloxane removal and electricity generation using internal combustion engine at Ames Water Pollution Control Facility (AWPCF), experiments were conducted to verify the possibility of using a patented micro-aeration H_2S removal technology. The experiments were conducted at two places—the Environmental Research Laboratory lab at Iowa State University (ISU) and the AWPCF. When the experiment was conducted at the lab, synthetic biogas (H_2S in helium) was used to simulate the H_2S-laden biogas while effluent from pilot-scale digester was used as medium for sulfide oxidizing unit (SOU). However, when at the AWPCF, real biogas and different types of water were used to as medium to feed to the SOU.

The primary objectives of the study were (1) to demonstrate an innovative, low-maintenance, low-cost, laboratory proven H_2S removal unit at AWPCF and (2) to collect full-scale design parameters i.e. sizing, air dosing rate, sulfide removal efficiency, and operating cost estimate for AWPCF. Addition to the primary objectives, a linear regression model was constructed to predict the concentration of output H_2S based on input H_2S concentration, biogas flow rate, and height of the SOU. A test to quantify the contribution of biotic/abiotic sulfide removal was also conducted.

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The study provides the potential cost effective solution to solve the siloxane removal problem encountered at AWPCF. The outcomes of this research would not only benefit the city of Ames in terms of cost savings, operator safety, etc. but all biogas-to-energy facilities in the nation.

METHODOLOGY

Sulfide oxidizing unit

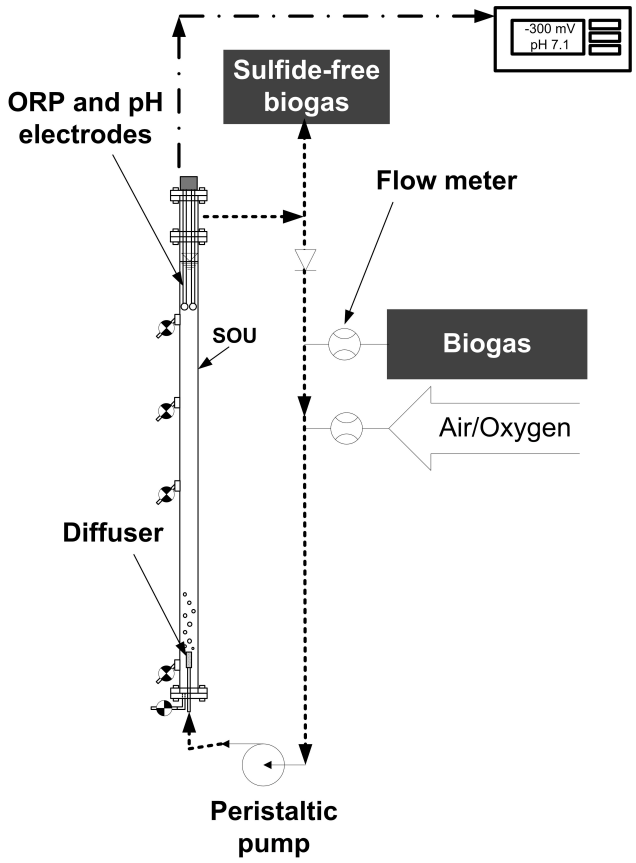

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Figure 1 – The schematic of the sulfide oxidizing unit.

A lab-scale sulfide oxidizing unit (SOU) used in this study was made up of several sections of Plexiglass tubes (ID 1.5 inch) to make height variation possible among 4, 6, and 8 ft (Figure 1). The bottom of the SOU was equipped with a medium bubble diffuser made by glass. pH and ORP electrodes are located on the top of the SOU. During the experiment, the tips of the electrodes were submerged in the medium at all time. The biogas and air entered the SOU through pumping by a peristaltic pump and exited at the top of the SOU. The SOU was operated as flow-through, meaning there was not recirculated. The SOU was tested on three liquid heights—3, 5 and 7.5 ft. At medium depths of 3, 5 and 7.5 ft, the SOU had active volume of 0.99, 1.65 and 2.50 L, respectively.

Liquid Media of Sulfide Oxidizing Unit

The AWPCF employs a two-stage trickling filter for wastewater treatment with a contact basin at the downstream to provide additional aeration. The first stage filter is designed for BOD removal while the second stage filter is designed for ammonia removal via nitrification process.

Four different types of media were chosen. This included (1) pilot-scale digester effluent, (2) plant effluent, (3) mixed liquor from biological treatment unit, and (4) digester supernatant. The pilot-scale digester effluent was obtained from a 92-L digester operated fed with synthetic organic waste with organic loading rate of 1.2 g-COD/-day (Duangmanee *et al*., 2009). The plant effluent was obtained from an effluent storage tank in the influent pumping station (wet well) while the mixed liquor and digester effluent were obtained from the contact basin, and a

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top sampling port of the secondary anaerobic sludge digester, respectively. Table 1 shows the characteristics of the medium. The alkalinity of the plant effluent and mixed liquor were low, which was likely the result of the nitrification process employed at the plant.

Table 1 – Characteristics of the medium.

	Pilot-scale digester effluent	Plant effluent	Mixed liquor	Digester supernatant
pH	7.24	5.83	6.92	7.53
Alkalinity, mg/L as CaCO3	4,800	75	160	3,100
Total Solids (TS), g/L	4.95	0.45	3.06	8.40
Total Suspended solids (TSS), g/L	0.96	0.05	2.42	6.86

To quantify the contribution of chemical sulfide oxidation, an abiotic sulfide removal study was conducted. In this test, the digester supernatant, autoclaved at 121 °C for 30 min, was used as a medium. Prior to each experiment, the different types of medium were fed through a sieve with opening size of approximately 1 mm to prevent clogging in the SOU.

Biogas characteristics

At the lab, H_2S in helium was used as synthetic biogas. The synthetic biogas was fed to the SOU from three different tanks with H_2S concentration of 1000, 2000, and 3000 ppmV. At the AWPCF, biogas was obtained from anaerobic digesters fed with waste activated sludge (WAS) and primary sludge. During the experimental period, H_2S concentrations were between 260 and

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650 ppmV. The biogas consisted of the following constituents: CH_4 59%, CO_2 39%, and N_2 2%.

Short-term experiment

The first short-term experiment was a series of H_2S removal tests conducted at ISU. The tests employed the use of various liquid heights of the SOU of 3, 5, and 7.5 ft, inlet H_2S concentrations of 1000, 2000, and 3000 ppmV, and H_2S loading rates of 0.83, 1.65, and 2.48 g/day. The inlet H_2S concentrations were chosen since they cover the range of H_2S concentrations from typical digesters, treating both municipal sewage sludge and agriculture wastes. All the tests in the experiment were conducted at an operating pH of 7.5 by periodically adding either 6N HCl or NaOH to maintain the pH. The gas mixture of H_2S and helium was used in this experiment to supply H_2S at various concentrations. Air was injected into the SOU at a sufficient rate so that a target output H_2S concentration of less than 10 ppmV could be achieved. Regardless of output H_2S concentration, air injection rate would stop if it resulted in an off-gas O_2 concentration exceeding 2%. From each test, the lowest outlet H_2S concentration with minimum airflow rate was reported.

The second short-term experiment was conducted in a pumping station at the AWPCF, using biogas produced from the anaerobic digesters. Three different types of liquid media were used to find optimal operating conditions to maximize H_2S removal efficiency. The operating parameters included operating pH, ORP, biogas flow rate, airflow rate, and the medium height of the SOU. During the experiment, off-gas H_2S concentration, and O_2 concentration were monitored. The experiment consisted of several sets of tests. In each set of tests, one set of

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operating pH, liquid height, and type of medium was chosen. The operating pH was adjusted by adding sodium bicarbonate to increase alkalinity until the desired operating pH was reached. This was an equilibrium pH resulted from a carbonate system—CO_2 in biogas and carbonate species in medium. After alkalinity addition, tested medium was pumped into the SOU. Then, biogas and air were pumped into the SOU at different flow rates, biogas flow varied from 77 to 896 ml/min and airflow varied from 4 to 179 ml/min. The airflow rates were adjusted to meet either 5, 10, or 20% of biogas flows. During the experiment, H_2S concentrations in biogas varied from 260 to 651 ppmV. Every set of the tests in short-term experiment lasted approximately 6-8 hours.

Validation experiment

After conducting series of short-term and long-term experiments, validation experiment was conducted at the Environmental Research Laboratory at ISU, using the digester supernatant as the medium. Unlike the short-term and long-term experiments, the validation experiment used a H_2S in helium, instead of real biogas. Since H_2S in the biogas at the AWPCF was never higher than 700 ppmV, the use of higher concentrations in this experiment would ensure the worst-case scenario of a typical municipal sludge digester. The experiment consisted of several tests of which their operating pH (7.0 and 7.5) levels and liquid heights (5 and 7.5 ft) were varied. The operating pH of the SOU was controlled by either adding 6 N of HCl or NaOH. The validation experiment was conducted at room temperature (25-28 °C) whereas the short-term and long-term experiments were conducted at 15 °C or less. Biogas flow rates were varied from 300 to 1490 ml/min with H_2S concentration of 1000 ppmV. Airflow rate was 10% that of biogas. Because of

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the difference of sampling dates, the digester supernatant in this test had TS and TSS of 26.9 and 26.1 g/L, respectively.

Analytical methods

The following parameters were analyzed in liquid samples: pH, oxidation reduction potential (ORP), temperature, total solids (TS), total suspended solids (TSS), dissolved sulfide, insoluble sulfide, sulfate, thiosulfate, and elemental sulfur. In gas sample, the following parameters were tested: methane (CH_4), carbon dioxide (CO_2), nitrogen (N_2), oxygen (O_2), and, hydrogen sulfide (H_2S). TS, TSS, dissolved sulfide, and insoluble sulfide were determined according to the Standard Methods (APHA, 1995). CH_4, CO_2, and N_2 were tested by using gas chromatography (GOW-MAC Series 350) equipped with a thermal conductivity detector (TCD) and fitted with a 84-mm (3.3-in.) stainless-steel column packed with Porapak T (60/80 mesh) (GOW-MAC Instrument Company, Bethlehem, PA, USA). Helium was used as the carrier gas at a flowrate of 35 mL/min. The temperatures of the injection port, oven, and detector were at 150, 50, and 100°C, respectively. H_2S and O_2 were determined by a multi-gas detector (BW defender Multi-Gas D4-2002-SP, BW Technologies, Arlington, TX, USA), colorimetric gas detection tubes (RAE Systems, San Jose, CA), or gas chromatography (GOW-MAC Series 400) equipped with TCD fitted with Chromosil '310 and Molesieve 18 80/100 (8 ft) column. Helium was used as the carrier gas at flow rate of 30 ml/min. The temperatures of the injection port, oven, and detector were at 100, 60, and 115°C, respectively. Gas flows were measured by several rotameters (Flow line Options, Macedonia, OH) calibrated for different types of gas. Sulfate and thiosulfate were analyzed by ion chromatograph (Dionex model DX 500, Dionex Cooperation,

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Sunnyvale, CA, USA) with AN1 anionic column (Varian Inc., Palo alto, CA, USA), and ASRS® ULTRA II, 4 mm, suppressor (Dionex P/N 061561) at 50 mA suppressor conductivity. Sodium carbonate/biocarbonate eluent (1.8/1.7 mmole/L) was used as mobile phase at a flow rate of 1 ml/min. Elemental sulfur was quantified by mass balance approach (Krishanakumar *et al*., 2005). pH and ORP was monitored through pH/ORP controller (Consort R305, Consort nv, Belgium).

RESULTS AND DISCUSSION

Short-term experiment

Sulfide removal at high loading rate. The first short-term experiment was conducted at the Environmental Research Laboratory lab at ISU. This experiment consisted of 27 tests, subjected to the variations of input H_2S concentrations (1000, 2000, and 3000 ppmV), liquid heights (3, 5, and 7.5 ft), and H_2S loading rate (0.83, 1.65, and 2.48 g/day). H_2S loading rates were normalized to volumetric H_2S loading rates by dividing the loading rates by reactor volumes (0.99, 1.70, and 2.50 L) at different liquid heights (3, 5, and 7.5 ft, respectively).

Figure 2 shows the effects of H_2S loading rate, input H_2S concentration, and liquid height on H_2S removal efficiency. At all liquid heights, increases in H_2S loading rates would result in decreases in H_2S removal efficiencies. To maintain the same H_2S loading rate with lower H_2S concentrations, gas flow rates had to be increased. By so doing, H_2S removal efficiencies at the same H_2S loading rate were lower at H_2S concentrations of 1000 or 2000 than at 3000 ppmV. In

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the tests with 5-ft SOU, the H_2S removal efficiencies at inlet H_2S concentration of 3000 ppmV were 99 and 97% for volumetric H_2S loading rates of 0.97 and 1.46 kg/m^3-day, respectively. However, the efficiencies were reduced to 79 and 53% for the same volumetric loading rate (Figure 2a and 2c) at inlet H_2S concentration of 1000 ppmV. This indicated that the SOU was more sensitive to the change in biogas flow rates than the change in H_2S concentrations at the inlet. The maximum volumetric H_2S removal rate obtained from the experiment was 1.41 kg/m^3-day (58.7 g/m^3-hr) at liquid height of 5 ft, volumetric H_2S loading rate of 1.46 kg/m^3-day (60.8 g/m^3-hr), and inlet H_2S concentration of 3000 ppmV. However, to maintain the off-gas H_2S concentration to be less than 10 ppmV, the maximum volumetric H_2S loading rate cannot exceed 0.49, 0.48, and 0.99 kg/m^3-day (20.3, 20.3, and 41.3 g/m^3-hr) for inlet H_2S concentration of 1000, 2000, and 3000 ppmV at medium heights of 5, 5 and 7.5 ft, respectively.

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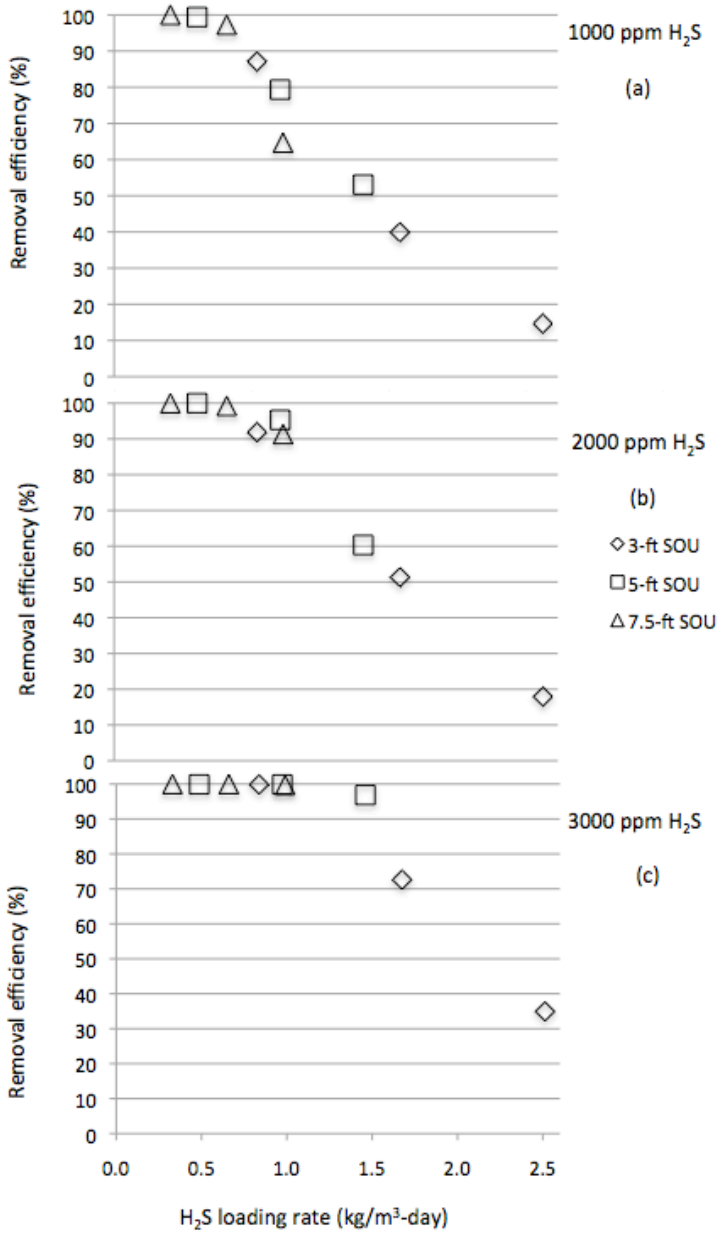

Figure 2 – Effects of H_2S loading rate, input H2S concentration, and liquid height on H_2S removal efficiencies.

Since H_2S concentration from anaerobic digesters at the AWPCF would never surpass 1000 ppmV, from the experiment, it is suggested that the SOU can be fed with biogas up to 15.9 m^3/m^3-hr when operated at 5-ft liquid height for outlet H_2S concentration of less than 10 ppmV

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at operating pH of 7.5. However, if it is preferred to have outlet H_2S concentration of less than 1 ppmV, the SOU can be fed with biogas up to 10.8 m^3/m^3-hr when operated at 7.5-ft liquid height at pH of 7.5.

Since ORP is related to the amount of oxygen and sulfide in the medium, it can be used as a controlling parameter for micro-aeration for sulfide removal (Duangmanee and Sung, 2009). To ensure that the off-gas H_2S concentration stayed below 10 ppmV, the experiment suggested the ORP be more than approximately -220 mV when the operating pH was 7.5 (Figure 3). This can be achieved by providing sufficient oxygen (or air) for sulfide oxidation.

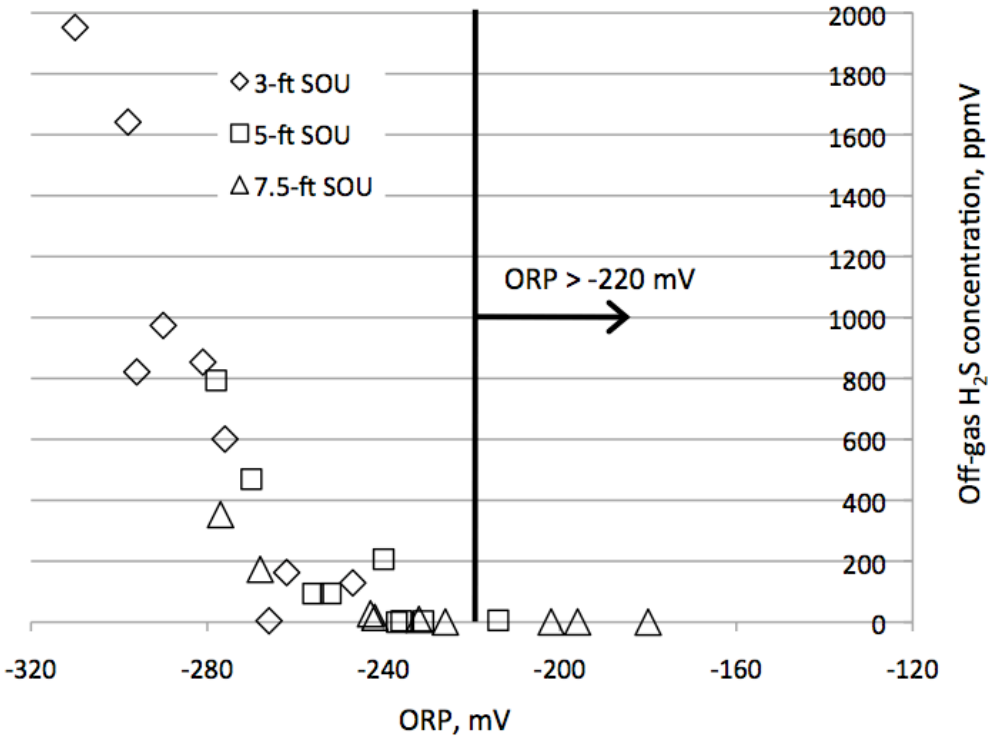

Figure 3 – A Plot between ORP and off-gas H_2S concentration at pH = 7.5.

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Generalized Linear Model

A Generalized Linear Model (GLM) was used to model the relationship between the hydrogen sulfide output concentrations, the liquid height of SOU, the hydrogen sulfide input concentration, the flow rate, and the loading rate. The descriptive statistics, Pearson correlation and regression analysis were performed using the data collected from the experiments. In the linear regression analysis, the hydrogen sulfide output concentration (H_2S) is considered the dependent variables whereas the flow rate (F), the hydrogen sulfide input concentration (C), and the liquid height (H) of SOU are the explanatory variables. The descriptive statistics and the Pearson correlation of dependent and explanatory variables are provided in Table 2 and 3, respectively.

Table 2 – Descriptive Statistics.

	Mean	Unit	Std. Deviation
Hydrogen sulfide output concentration (H_2S)	347.926	ppmV	520.880
Liquid height (H)	5.167	ft	1.876
Hydrogen sulfide input concentration (C)	2000.000	ppmV	882.060
Flow rate (F)	550.000	ml/min	362.085

Table 3 – Pearson Correlation.

		H_2S	H	C	F	$H*C$	$H*F$	$C*F$
Pearson correlation	H_2S	1.000	-0.566	0.021	0.279	-0.386	-0.045	0.535
	H	-0.566	1.000	0.000	0.000	0.635	0.461	0.000
	C	0.021	0.000	1.000	-0.689	0.728	-0.576	0.000
	F	0.279	0.000	-0.689	1.000	-0.502	0.836	0.632
	$H*C$	-0.386	0.635	0.728	-0.502	1.000	-0.180	0.000
	$H*F$	-0.045	0.461	-0.576	0.836	-0.180	1.000	0.528
	$C*F$	0.535	0.000	0.000	0.632	0.000	0.528	1.000
Sig. (1-tailed)	H_2S	.	0.001*	0.458	0.080	0.023*	0.411	0.002*

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H	0.001*	.	0.500	0.500	0.000*	0.008*	0.500
C	0.458	0.500	.	0.000*	0.000*	0.001*	0.500
F	0.080	0.500	0.000*	.	0.004*	0.000*	0.000*
*H*C*	0.023*	0.000*	0.000*	0.004*	.	0.185	0.500
*H*F*	0.411	0.008*	0.001*	0.000*	0.185	.	0.002*
*C*F*	0.002*	0.500	0.500	0.000*	0.500	0.002*	.

At 95% confidence level, the Pearson correlation indicates that there is a significant relationship between hydrogen sulfide output concentration (H_2S) and liquid height (*H*). For the predictors flow rate (*F*) and hydrogen sulfide input concentration (*C*), although their individual correlations to hydrogen sulfide output concentration (H_2S) were not found significantly, their effect size was show up through their interaction (*C**F*). Moreover, the interaction of liquid height (*H*) and the hydrogen sulfide input concentration (*C*) is significantly related with the hydrogen sulfide output concentration (H_2S).

To model a multivariate regression models, besides four main independent predictor variables (i.e., H_2S, *F*, *C* and *H*), the products of different explanatory variables (i.e., interaction terms) were also included in the regression analysis. Adding the interaction terms into the regression analysis can greatly expand understanding of the relationships among the variables in the model.

Table 4 – Model Summary.

Model	Sum of Squares	Df	Mean Square	F	Sig.
Regression	4959973	6	826662.2	7.895	0.000
Residual	2094243	20	104712.1		

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Total	7054216	26
R Square	0.703	

Table 5 – Coefficients.

Model	Coefficients	T	Sig
(Constant)	-1289.657	-1.315	0.203
H	241.516	1.375	0.184
C	0.533	1.572	0.132
F	0.788	0.938	0.360
*H**C*	-0.130	-2.278	0.034[a]
*H**F*	-0.251	2.284	0.070[a]
*C**F*	0.001	-1.912	0.006[a]

[a] indicates the significant regression coefficients at 95% confidence level.

Results from the regression analysis showed in Tables 4 and 5 indicate that the flow rate, the interaction between the liquid height of SOU and the flow rate, the interaction between and the hydrogen sulfide input concentration, and the interactions among the three main independent variables significantly determine the magnitude of the hydrogen sulfide output concentration. With the coefficient from table 11, a regression equation can be formulated as:

$$H_2S = -1289.657 + 241.516H + 0.533C + 0.788F - 0.130HC - 0.251HF + 0.001CF.$$

Since the interaction of the flow rate and the hydrogen sulfide input concentration (*C**F*) can also be described in term of the loading rate (*L*), the equation can be rewritten as:

$$H_2S = -1289.657 + 241.516H + 0.533C + 0.788F - 0.130HC - 0.251HF + \frac{0.001L}{\mathrm{k}}$$

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where k is a constant value at a specific operating temperature and atmospheric pressure.

At the operating temperature of 25°C and pressure 740 mmHg, k = 1.834×10^{-6}, therefore the GLM to predict the hydrogen sulfide output concentration (H_2S) when the operating temperature of 25°C and pressure at 740 mmHg is:

$$H_2S = -1289.657 + 241.516H + 0.533C + 0.788F - 0.130HC - 0.251HF + 545.256L$$

Where

H_2S = hydrogen sulfide output concentration (ppmV)

H = liquid height (ft)

C = hydrogen sulfide input concentration (ppmV)

F = flow rate (ml/min)

L = loading rate (g/day)

The regression equation expresses the best predictor of the hydrogen sulfide output concentration (H_2S), given the liquid height (H), the flow rate (F), the hydrogen sulfide input concentration (C) and the loading rate (L). The R Square of 0.703 indicates that approximately 70.3% of the variability of the hydrogen sulfide output concentration (H_2S) is accounted for by the liquid height (H), the flow rate (F), the hydrogen sulfide input concentration (C), the loading rate (L), and their interaction terms. The regression also suggests that the change in the loading rate has the most effect on the change in hydrogen sulfide output concentration followed by the change of

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the liquid height, the change of the flow rate, the change in the hydrogen sulfide input concentration, the change in the interaction of the liquid height and the flow rate, and finally the change in the interaction of the liquid height and the hydrogen sulfide input concentration. Moreover, at a given load rate and height, the change in flow rate (*F*) has more effect on the change in level of the hydrogen sulfide output concentration (H_2S) than the change of hydrogen sulfide input concentration (*C*).

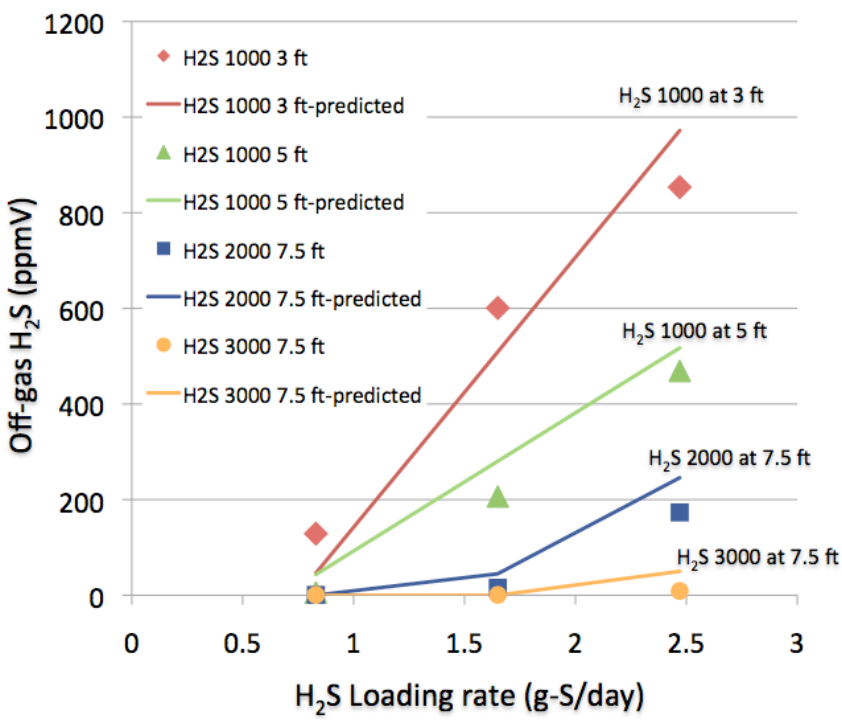

Figure 4 – Plots between experimental and predicted off-gas H_2S concentrations.

By assuming the negative calculated off-gas H_2S concentrations equal to zero, the experimental and predicted values are plotted against H_2S loading rate (Figure 4). It can be seen that the experimental values were in close agreement with the predicted values, suggesting that the regression equation could be used to predict the off-gas H_2S concentration at the given

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conditions.

Sulfide removal with various media. The second short-term experiment was conducted at the AWPCF. The experiments started with conducting series of sulfide removal tests examining the feasibility of using several types of media available at the AWPCF, namely plant effluent, mixed liquor, and digester supernatant. The main goal was to reduce off-gas H_2S concentration to < 10 ppm with off-gas O_2 < 2%. The plant effluent was chosen due to a study in the laboratory at ISU, which suggested that significant sulfide removal could occur even when distilled water was used as medium (data not shown). In addition the plant effluent is readily available and is easy to be disposed at the AWPCF. A sulfide removal mechanism may be contributed from chemical and biological oxidations. Previous researches suggested that biological contribution was a majority when sulfide concentration is low (Buisman *et al.*, 1990b). However, as sulfide concentration increases, the sulfide oxidation will be shifted towards the chemical one. At the AWPCF, the sulfide concentration in biogas is < 1000 ppmV. Therefore, adding mixed liquor that contained sulfide oxidizing bacteria to the medium would likely to add biological contribution to the overall sulfide oxidation. Furthermore, some trace metals can serve as catalysts for sulfide oxidation (O'Brian and Birkner, 1977). Heavy metals, such as Fe, Ni, Cu, Zn, Mn, and Co, are known to precipitate sulfide (Lewis and van Hille, 2006; Poulton *et al.*, 2002; Nedwell and Reynold, 1996). As a result, digester supernatant that contains many trace metals may be a good candidate for sulfide oxidation by micro-aeration.

Even though the experiment was conducted at three different percentages of airflow rates, only results at 10% air-to-biogas flow rate are shown in Table 2. When alkalinity was not altered, the

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operating pHs of the SOU when using plant effluent, mixed liquor, and digester supernatant were approximately 5.25, 5.65, and 6.75, respectively. Because of the low operating pH, H_2S removal efficiencies were not enough to reduce the off-gas H_2S concentration to < 10 ppmV throughout the examined flow rates. When the operating pHs were increased to 7.0 and 7.5, the H_2S removal efficiencies increased to as much as 79.5 and 96.0% for plant effluent and mixed liquor, respectively. However, the off-gas H_2S concentration still could not meet the target of < 10 ppmV. When using digester supernatant as medium, H_2S removal efficiencies improved greatly. Up to 99.9% of H_2S removal efficiency could be achieved with off-gas H_2S concentration of < 1 ppmV and O_2 of < 2%. When the SOU was operated at pH of 7.2, the lowest off-gas H_2S concentration (9 ppmV) was obtained at the biogas flow rate of 218 ml/min. However, the highest H_2S loading rate of 0.36 kg/m^3-day (15.0 g/m^3-hr) could be achieved while the off-gas O_2 concentration was 0.7% when the SOU was operated at pH of 7.5. In this case, the H_2S concentration was merely 12 ppmV.

Table 6 – Performance of the SOU when using plant effluent, mixed liquor, or digester supernatant as medium at liquid height of 7.5 ft and air at 10% of biogas flow rate

Medium	Operating pH	ORP (mV)	Biogas flow (ml/min)	H_2S (ppmV)		% removal	O_2 (%)
				Inlet	Outlet		
Plant Effluent (No pH adjustment)	5.26	-77	77	260	128	**51.0**	1.7
	5.26	-84	135	260	185	**29.0**	2.1
	5.27	-81	219	260	197	**24.5**	2.5
	5.25	-88	517	279	233	**16.3**	2.1
	5.27	-88	896	279	251	**10.0**	2.1
Plant Effluent (pH = 7.0)	6.99	-195	218	361	148	**58.9**	1.9
	6.99	-206	517	361	202	**43.9**	1.9
	6.99	-211	896	361	221	**38.6**	1.9

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Plant Effluent	7.54	-195	218	357	73	**79.5**	2.3
(pH = 7.5)	7.53	-202	517	357	158	**55.6**	1.3
	7.54	-206	896	357	163	**54.4**	1.3
Mix liquor	5.68	-92	218	477	319	**33.2**	1.3
(No pH adjustment)	5.66	-96	517	477	345	**27.6**	0.9
	5.63	-95	896	477	354	**25.8**	0.7
Mix liquor	7.01	-203	218	506	255	**49.6**	1.3
(pH = 7.0)	6.98	-207	517	506	286	**43.5**	0.9
	6.97	-208	896	506	330	**34.8**	0.7
Mix liquor	7.55	-201	218	480	19	**96.0**	0.9
(pH = 7.5)	7.54	-224	517	480	59	**87.7**	0.9
	7.52	-240	896	480	130	**72.9**	0.7
Digester Supernatant	6.78	-147	218	378	72	**81.0**	1.1
(No pH adjustment)	6.76	-164	517	378	143	**62.2**	0.7
	6.73	-168	896	378	181	**52.2**	0.9
Digester Supernatant	7.25	-143	218	444	9	**98.0**	1.3
(pH = 7.2)	7.19	-175	517	444	53	**88.1**	0.7
	7.18	-190	896	444	94	**78.8**	0.7
Digester Supernatant	7.57	-109	218	530	<1	**99.9**	1.3
(pH = 7.5)	7.54	-134	517	530	3	**99.4**	0.7
	7.52	-166	896	530	12	**97.7**	0.7

Abiotic and biotic sulfide oxidation. To quantify abiotic and biotic contribution for sulfide oxidation, two tests were conducted using two types of media. One medium was obtained from digester supernatant after alkalinity addition. The other medium also came from digester supernatant but after autoclaving to suppress biological activity and followed by adjustment of alkalinity. The two tests were conducted using approximately the same H_2S concentrations (530-550 ppmV) and operating pH (7.5). Figure 5 shows the contribution of abiotic/biotic sulfide removal. The H_2S removal rates were adjusted so that the H_2S loading rates of abiotic and biotic tests were equal. It can be seen that the majority of sulfide oxidation was due to abiotic oxidation (or chemical oxidation). At the biogas flow rate of 896 ml/min and airflow at 10%, H_2S removal rate obtained from using non-autoclaved digester supernatant was 0.36 kg/m^3-day (15.2 g/m^3-hr); however, the sulfide removal rate from autoclaved supernatant was 0.35 kg/m^3-day (14.4 g/m^3-hr). This indicates that the overall sulfide removal was contributed

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approximately 95% from abiotic oxidation.

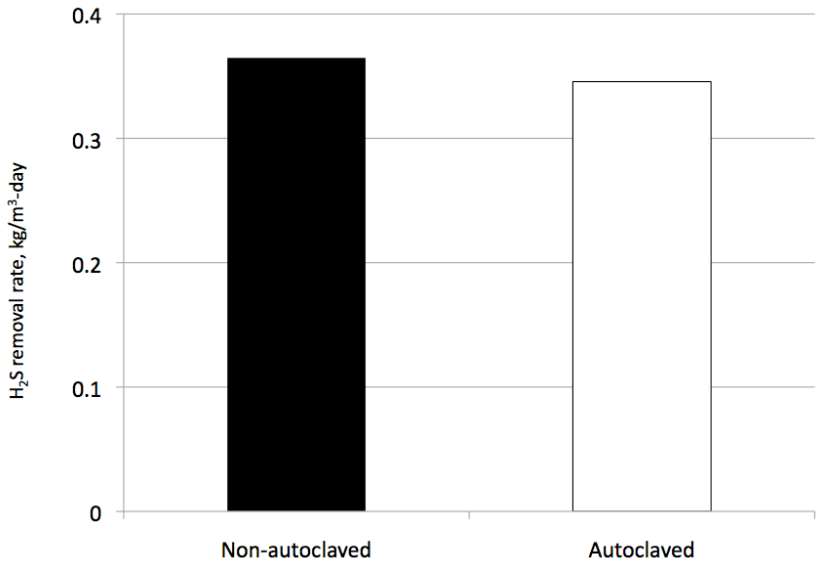

Figure 5 – H_2S removal rate for abiotic/biotic H_2S removal tests.

Long-term operation of SOU

After conducting the short-term experiment, the operating parameters (biogas flow rate, airflow rate, operating pH, type of liquid media, and liquid height) were chosen for the long-term study. The parameters that yielded the highest removal rate with H_2S and O_2 concentration < 10 ppmV and 2%, respectively, were selected. Consequently, in the long-term experiment, the SOU received a biogas flow rate of 706 ml/min with 10% airflow and operated at pH of 7.5 with liquid height of 7.5 ft.

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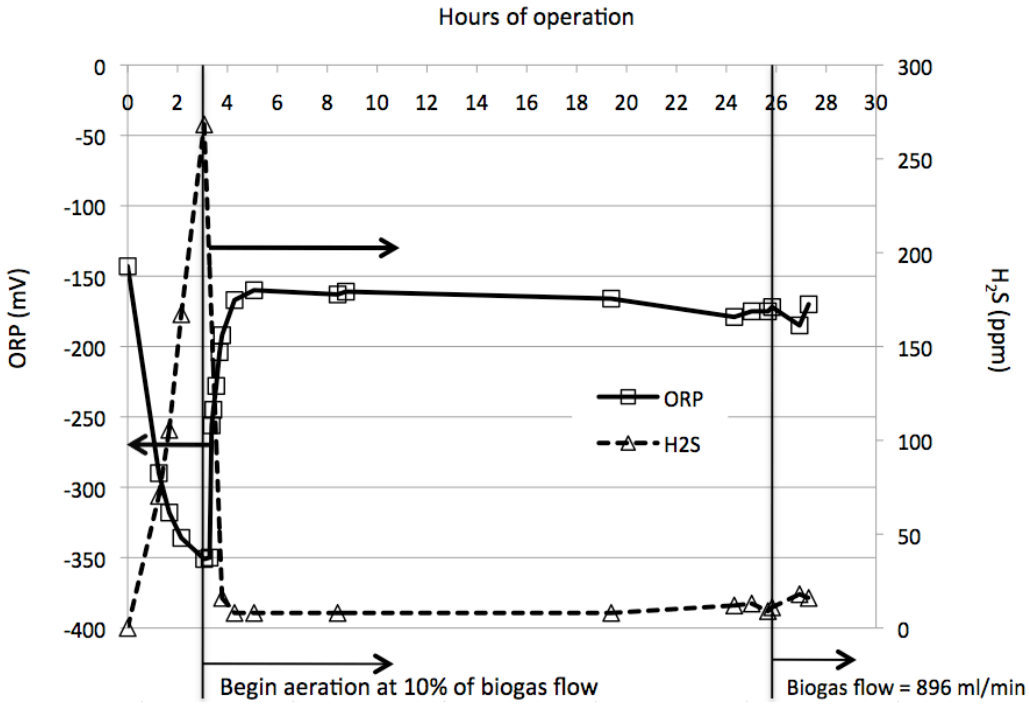

Figure 6 – Profile of ORP and Off-gas H_2S concentration of long-term experiment

The ORP and H_2S concentration profiles in off-gas were shown in Figure 6. During the first three hours of the experiment, only biogas with average H_2S concentration of 620 ppm was injected into the SOU, resulted in an increase in H_2S concentration in the off-gas from 0 to approximately 260 ppm with a decrease of ORP to -350 mV. Then, air was injected into the SOU at the rate of 10% of biogas flow rate. Only about 30 min after air injection, H_2S concentration in the off-gas was reduced from 270 to 8 ppmV, coinciding with an increase of ORP to -160 mV. Throughout the test, O_2 concentration was between 0.7-1.3%. The ORP and H_2S concentration stayed near the level for approximately 24 hours. After 24 hours of aeration,

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the biogas flow rate was increased by approximately 30% to 896 ml/min. As a result, the ORP decreased to -185 mV with off-gas H_2S concentration of 18 ppmV. In an attempt to reduce outlet H_2S concentration, airflow rate was increased to 20% of biogas. However, outlet H_2S concentration only decreased to 13 ppmV.

After the test, liquid samples were periodically drawn from the SOU for dissolved sulfide, insoluble sulfide, sulfate, and thiosulfate. The amount of elemental sulfur was estimated by mass balance subtraction technique. The quantities of all sulfur species are normalized to report in terms of sulfur (Figure 7).

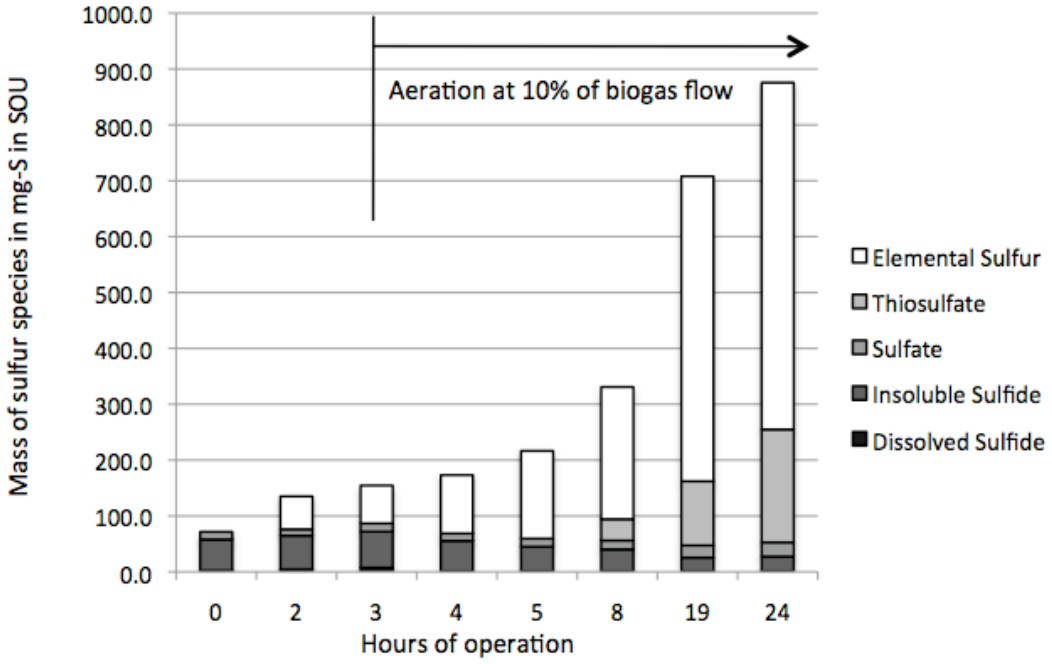

Figure 7 – Sulfur mass balance during the long-term experiment.

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Since the SOU was not deprived of O_2 prior to the start up, some element sulfur was formed during the first two hours of biogas injection; however, only slight change of elemental sulfur was found prior to air injection. During the period, some of the H_2S dissolved in to the medium, increased the concentration of dissolved sulfide, and elevated the H_2S concentration in the off-gas. The amount of insoluble sulfide increased from 22 to 26 mg/L, indicating the binding of sulfide with trace metals in the medium. After air injection, the concentration of dissolved and insoluble sulfides decreased to approximately 0.5 and 17 mg/L, thereby reducing the off-gas concentration of H_2S to < 10 ppmV within about 30 min. Significant amount of elemental sulfur was formed after aeration. It was estimated that the elemental sulfur was formed at the rate 0.25 kg/m^3-day, and by the end of the experiment, over 70% of sulfur species was elemental sulfur. Dissolved sulfide, insoluble sulfide, sulfate, and thiosulfate constituted approximately 0.1, 3.0, 3.0, 23.0%, respectively. It was also interesting to note that not until the 8th hour of the experiment did the thiosulfate and sulfate begin to form. These formations may be the result of the oxidation of elemental sulfur accumulated inside the SOU.

Validation experiment

The validation experiment was conducted at ISU, using digester supernatant obtained from the AWPCF. The SOU with liquid height of 5 and 7.5 was used in the study. Two pH levels, 7.0 and 7.5, were chosen as operating pHs. When the SOU was operated at pH of 7.0, no alkalinity was adjusted since the exiting alkalinity (approximately 5,000 mg/L as $CaCO_3$) could maintain the operating pH. In fact, when the biogas has CO_2 of approximately 40%, the operating pH should have been close to 7.3 based on the relationship among operating pH,% of CO_2 in biogas,

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and alkalinity as described by Parkin and Owen, 1986. However, for conservative approach, the pH of 7.0 was used in the test.

Table 7 – Performance of the SOU when using digester supernatant at liquid height of 5 and 7.5 ft and pH of 7.0 and 7.5, performed at temperature of 25-28°C.

Medium	Operating pH	ORP	Biogas flow (ml/min) ml/min	Sulfide (ppm) inlet	Sulfide (ppm) Outlet	% removal
pH = 7.0 at 7.5 ft	7.00	-148	675	1000	<1	**99.9**
	7.01	-164	900	1000	9	**99.1**
	6.99	-215	1350	1000	83	**91.7**
pH = 7.0 at 5 ft	6.99	-266	300	1000	21	**97.9**
	7.01	-259	450	1000	56	**94.4**
	7.01	-242	900	1000	133	**86.7**
pH = 7.5 at 7.5 ft	7.50	-128	900	1000	3	**99.7**
	7.50	-179	1350	1000	2	**99.8**
	7.50	-183	1490	1000	3	**99.7**
pH = 7.5 at 5 ft	7.51	-190	900	1000	3	**99.7**
	7.52	-239	1350	1000	17	**98.3**
	7.51	-241	1490	1000	32	**96.8**

Table 7 shows the performance of the SOU in this experiment. It can be seen that the sulfide removal efficiencies of the test conducted at ISU were significantly higher than those conducted at the AWPCF (Table 6). Since the experiment was conducted at the Environmental Research Laboratory, it was performed at temperature of 25-28 °C (compare to 8-15 °C at the AWPCF). Furthermore, TSS content of digester supernatant was approximately 26.1 g/L, which was significantly higher than 8.4 g/L used in the other experiment. The digester supernatant with higher TSS would likely to have higher contents of trace metals. The higher temperature and higher concentrations of trace metals would allow higher sulfide removal efficiency and rate, which also allow lower H_2S concentration in the off-gas (compare to Table 6).

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When operated at pH of 7.0, the SOU with liquid height of 7.5 ft could receive biogas up to 900 ml/min and still meet the target off-gas H_2S concentration of < 10 ppmV with O_2 of < 2%. However, if the operating height of 5 ft is required, the operating pH must be 7.5 to meet the targets at biogas specific flow rate of 900 ml/min (21.6 m^3/m^3-hr). Lastly, if the high biogas flow rate is priority, then the liquid height and operating pH need to be 7.5 ft and 7.5, respectively. Up to 1490 ml/min (35.8 m^3/m^3-hr) of biogas specific flow can be maintained, and the target is still met. Table 8 sums up the requirements and solutions to meet the target.

Table 8 – H_2S loading rate to meet the targets (H_2S < 10 ppmV and O_2 < 2%) at different requirements.

Requirements	Minimum Operating pH	Minimum Liquid height (ft)	Maximum specific flow rate (m^3/m^3-hr)	H_2S loading rate (kg/m^3-day)
No pH adjustment required	7.0	7.5	21.6	0.66
Height of 5 ft required	7.5	5	21.6	1.00
High flow rate required	7.5	7.5	35.8	1.09

Operating cost and other requirements

The anaerobic digester at the AWPCF produces approximately 50,000 ft^3/day (approximately 35 cfm or 60 m^3/hr) with H_2S concentration < 1000 ppmV. The assumption was made for the operation to be robust, low-maintenance, low-cost, easy-to-operate; therefore, the adjustment of

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alkalinity will not be suitable for the operation at the plant. The design without alkalinity addition can handle H_2S loading rate up to 0.66 kg/m^3-day (27.5 g/m^3-hr) at a liquid height of 7.5 ft and operating pH of 7.0. The digester supernatant with alkalinity approximately 5000 mg/L as $CaCO_3$ and TSS of 26 g/L will be used as medium. The operating temperature needs to be approximately 25°C; therefore, insulation is needed.

Required reactor volume. H_2S loading rate is estimated by the following equations:

$$Mp/Va = \frac{ppmV \cdot GMW \cdot 1000L/m^3}{22.414 \cdot (\frac{T_2}{273K}) \cdot (\frac{101.325}{P_2})}$$

where Mp = micro-gram, GMW = molecular weight = 32 g/mole, Va = 1 m^3, T_2 = Operating temperature (°K) = 298 °K, P_2 = Operating pressure (kPa) = 98.658 kPa, and ppmV = Concentration of H_2S = 1000 ppmV. H_2S loading rate of 1.82 kg-S/day can be obtained by multiplying H_2S concentration (kg-S/m^3) with biogas flow rate (m^3/day). The required volume can be calculated by dividing the H_2S loading rate by volumetric loading rate (kg-S/m^3-day) from the experiment. The resulting required volume is approximately 3 m^3. For 7.5-ft SOU, the inside diameter needs to be 4.5 ft to obtain the active volume of 3.4 m^3

Medium replacement for maintaining pH. The requirement for medium replacement was estimated using worst-case scenario when H_2S dissolved into the medium and turn into SO_4^{2-} during H_2S removal.

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$$H_2S \leftrightarrow HS^- + H^+$$

$$2HS^- + O_2 \rightarrow 2S + 2OH^-$$

$$2HS^- + 4O_2 \rightarrow 2SO_4^{2-} + 2H^+$$

From the scenario, two moles of H^+ is formed per mole of H_2S dissolved. With alkalinity of 5000 mg/L as $CaCO_3$, the required medium replacement to maintain pH is approximately 0.05 m^3/hr.

Medium replacement for maintaining temperature. The requirement for medium replacement for temperature (25°C) was estimated by the following energy balance equation:

$$Q = m_{medium} Cp_{medium} (T_2 - T_1)_{medium} = m_{gas} Cp_{gas} (T_2 - T_1)_{gas}$$

Where m = mass of substance (g), Cp = heat capacity (J/g-°C), and T_2 - T_1 = temperature difference (°K). Heat capacity of gas mixture (1.30 J/g-°C) can be calculated by assuming that the biogas contains 54% of CH_4, 36% of CO_2, and 10% of air. Heat capacity of the medium is assumed to be equal to that of water (4.18 J/g-°C). The temperature of input medium and biogas were assumed to be 20°C and 43°C, respectively. Consequently, the required medium replacement to maintain temperature is approximately 0.08 m^3/hr.

Operating cost. The main operating cost will be electricity consumption of motor used to run a blower. It was estimated that a blower with 2.5 BHP could be used to pass biogas through the

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SOU at 35 cfm and 5 psi. Operating cost can be calculated from the following equation:

$$KW_{input} = \frac{BHP_{Blower} x 0.746}{Efficiency_{motor} \cdot Efficiency_{VFD}}$$

With motor efficiency of 85%, VFD efficiency of 97%, electricity cost of $0.10/KWhr, and 24-hour operation, the electricity cost is $5.43/day. With 99.1% H_2S removal efficiency, the cost for H_2S removal is $2.11/kg-S removed.

CONCLUSIONS

The SOU utilizes micro-aeration technique whereby small amount of air is injected into the reactor to selectively convert sulfide to elemental sulfur. From the experiment, a full-scale SOU with active volume of 3.2 m^3 at 7.5-ft liquid height can be installed at the AWPCF and remove up to 99% of H_2S in biogas at flow rate up to 60 m^3/hr (50,000 ft3/day) with maximum inlet H_2S of 1000 ppmV. The SOU requires no pH adjustment or chemical added. The operating cost per kg of sulfur removed is estimated to be about $2/kg-S removed. The increased metal contents and temperature of the medium was likely the reason for increased the H_2S removal rate. A generalized linear regression suggested that liquid height and flow rate significantly affected output H_2S concentration.

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CHAPTER 5. GENERAL CONCLUSIONS

General Discussion

It was demonstrated that hydrogen sulfide could be remove from the biogas by using micro-aeration controlled by oxidation-reduction potential (ORP). With integrating the sulfide oxidizing unit (SOU) with an anaerobic digester, both gaseous and aqueous sulfide can simultaneously be removed with 98% elemental sulfur production. By recycling the sulfide-free biogas (< 1 ppmV of hydrogen sulfide) back to the anaerobic digester, sulfide was removed as fast as it is produced without any change in methanogenic activity. This reactor system is a perfect candidate for alleviating a possible sulfide toxicity posted to the digester.

As controlling parameter, the ORP was able to control the amount to air injection to the SOU and prevent oxygen overdosing during unexpected surges of aeration by acting as dampener. With the SOU as standalone unit, this innovative sulfide removal technique was able to sustain high hydrogen sulfide loading rate but still maintain output hydrogen sulfide to be less than 10 ppmV with out oxygen less than 2%.

The SOU requires no media, nutrient or chemical addition since it uses the effluent from the digester as a medium for pH control and nutrient supplement. However, since ORP increases as the pH decreases and sulfide absorption and removal reduces alkalinity, the SOU requires medium replacement to maintain the pH and the control of aeration. The hydrogen sulfide in the biogas can be removed with a matter of hours. The rate and efficiency of sulfide removal by micro-aeration depends on operating liquid height, biogas flow rate, hydrogen sulfide concentration, and operating pH. However, a generalized linear regression

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suggested that liquid height and flow rate significantly have more effect on the output H_2S concentration. Since 95% of hydrogen sulfide removal was contributed from abiotic reaction, this sulfide removal is classified as chemical process. By increasing trace metal contents and temperature of the medium, the hydrogen sulfide removal rate was greatly improved. From this research, the maximum hydrogen sulfide was found to be approximately 1.0 kg/m^3-day. Operating cost was estimated to be approximately $2/kg-S removed.

Recommendations for Future Research

The future researches includes:

- **The effect of temperature variation:** From the experiment, it was suggested that low temperature adversely affected the hydrogen sulfide removal rate. On the other hand, the experiment in Thailand confirms that the alleviated temperature flavors the reaction rate (data not shown). The dilemma of the temperature is that the rise in temperature reduces hydrogen sulfide absorption but at the same time increases the reaction rate. However, the comparison experiment using the same conditions has not been conducted yet. Therefore, the systematically designed experiment focusing on temperature is needed.

- **The effect of metal species and their concentrations:** the presence of metal in the medium can catalyze the hydrogen sulfide removal. However, there has been no research realizing the effect of metals on micro-aeration yet. Consequently, this type of research is needed.

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- **The effect of shock loading:** Hydrogen sulfide concentration from anaerobic digester can be varied with the change in feed composition and quantity. The ORP can be used to control aeration rate and serve as dampener when instantaneous air injection rate was increased. However, the behavior of ORP and its ability to control aeration during the shock loading has not been studied. It will be a good assurance to know the effect of the shock loading of hydrogen sulfide.

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