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Comparing Hydrogen Sulfide Removal Efficiency in a Field-Scale Digester Using Microaeration and Iron Filters

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Abstract: Biological desulfurization of biogas from a field-scale anaerobic digester in Peru was tested using air injection (microaeration) in separate duplicate vessels and chemical desulfurization using duplicate iron filters to compare hydrogen sulfide (H_2S) reduction, feasibility, and cost. Microaeration was tested after biogas retention times of 2 and 4 h after a single injection of ambient air at 2 L/min. The microaeration vessels contained digester sludge to seed sulfur-oxidizing bacteria and facilitate H_2S removal. The average H_2S removal efficiency using iron filters was 32.91%, with a maximum of 70.21%. The average H_2S removal efficiency by iron filters was significantly lower than microaeration after 2 and 4 h retention times (91.5% and 99.8%, respectively). The longer retention time (4 h) resulted in a higher average removal efficiency (99.8%) compared to 2 h (91.5%). The sulfur concentration in the microaeration treatment vessel was 493% higher after 50 days of treatments, indicating that the bacterial community present in the liquid phase of the vessels effectively sequestered the sulfur compounds from the biogas. The H_2S removal cost for microaeration (2 h: \$29/m^3 H_2S removed; and 4 h: \$27/m^3 H_2S removed) was an order of magnitude lower than for the iron filter (\$382/m^3 H_2S removed). In the small-scale anaerobic digestion system in Peru, microaeration was more efficient and cost effective for desulfurizing the biogas than the use of iron filters.

Keywords: desulfurization; anaerobic digestion; biogas; sulfur-oxidizing bacteria; H_2S

1. Introduction

Anaerobic digestion (AD) reduces organic pollution while creating renewable energy in the form of methane (CH_4)-enriched biogas. However, the hydrogen sulfide (H_2S) concentration in biogas can be high, ranging from 100 to 30,000 ppm [1,2]. Sulfate-rich feedstocks, such as swine manure, can produce biogas with high H_2S concentrations, which affects the use of the biogas after digestion [3]. H_2S is originated by the microbial breakdown of organic material during the anaerobic digestion [4]. The presence of H_2S in biogas can corrode biogas system components (pipes, compressors, gas storage tanks, engine generator sets (EGS) for electricity production, and boilers) through the formation of corrosive sulfuric acid when water vapor is present [5,6]. The presence of H_2S can compromise the functions of EGS, produce odor prior to biogas utilization, and is toxic at high concentrations [7]. In addition, H_2S contaminants in advanced energy conversion equipment, such as fuel cells, can permanently foul the equipment [8]. According to the US Occupational Safety and Health Administration (OSHA), 0.01–1.5 ppm H_2S is the odor threshold (characteristic rotten egg smell), while 2–5 ppm H_2S may cause nausea and headaches, and 1000–2000 ppm H_2S can cause death, depending on the length of exposure.

Biogas purification has been researched in recent years to protect health and biogas utilization equipment [9]. While biogas desulfurization can be achieved using multiple methods, generally, H_2S removal methods can be divided into two groups: physical-chemical removal and biological removal using sulfur-oxidizing bacteria (SOB) [10]. Physical-chemical methods include adsorption, absorption, scrubbing, membrane separation, and precipitation, where chemicals are used to either bind and capture sulfur prior to H_2S formation or capture the H_2S molecule after formation [11]. The iron sponge process was implemented during the 19th century for H_2S removal and has been in use in Europe and the United States for over 100 years [12]. In Peru and areas with other low-cost digestion systems, a simple iron filtration system consists of a tank, usually a cylindrical tank or pipe, containing iron oxide in the form of iron sponges located between the digester and biogas utilization system [13]. The chemical bond between sulfur in the biogas and iron oxide occurs within an iron filter system at ambient temperature. Alkaline conditions are needed, with a pH value greater than 7.5 [5]. Shelford et al. (2019) asserted that for each kg of iron oxide (Fe_2O_3) present in the system, 0.56 kg of sulfide can be removed from the biogas as elemental sulfur, as shown below in Equation (1). Iron oxide can be regenerated by adding air (O_2), which prolongs the life of the media, as shown in Equation (2) [5]. However, after each regeneration, the filters lose approximately 30% of their effectiveness due to the obstruction by elemental sulfur, which reduces the volume of biogas that can be treated between filter changes [5,14]. Saturated iron sponge material (when H_2S is no longer removed and/or when the wood bark has deteriorated) can be burned (where permitted), landfilled, or spread on agricultural land [5].

$$\text{Formation of iron sulfide: } Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O \quad (1)$$

$$\text{Regeneration and formation of elemental sulfur: } Fe_2S3 + 3/2O_2 \rightarrow Fe_2O_3 + 3S \quad (2)$$

There are varying operational and maintenance costs associated with iron filter systems. Generally, physical-chemical removal methods have higher costs due to chemical acquisition, energy use associated with the regeneration of saturated materials, and disposal of secondary pollutants produced [15]. For example, the cost of using iron filters for H_2S removal (without regeneration) have been shown to vary from \$2.93/d for 3000 ppm H_2S removed at a 13.42 m^3/h biogas production rate from the manure of 100 lactating cows, to \$117.77/d for 3000 ppm H_2S removed at a 536.89 m^3/h biogas production rate from the manure of 4000 lactating cows [5]. When the adsorbent materials are saturated, the materials must be properly disposed of, which poses health and environmental risks [16]. The cost of iron filter use and disposal will vary based on the cost of the fresh material, revenue for any sulfur extracted, disposal costs of processed adsorbent, and transportation distance [17].

Schiavon et al. (2017) determined that a commercial reagent powder containing Fe-EDTA resulted in a high H_2S removal efficiency (99%), forming elemental sulfur through absorption [18]. Metallic wastes rich in Fe or metallic waste products, such as mining wastes or fly ash from thermo-electrical plants, have also been proposed as sulfide removal materials [19]. A recent study showed that corn stover and maple biochar impregnated with Fe added into an anaerobic digester significantly reduced H_2S production by up to 93.3% without affecting CH_4 production [20]. Electrochemically-assisted scrubbing and stripping of H_2S has also been shown [21]. However, many of these H_2S removal techniques may not be available for small-scale digester operators due to the high costs and the need for specialized knowledge and access to equipment and absorbent materials [15], which reinforces the need for low-cost and easy-to-operate H_2S removal techniques for small-scale digester operators.

Biological-based H_2S removal methods include biotrickling filters (BTF), biofiltration, bioscrubbers, and air injection [10,22]. Bio-desulfurization is based on the inoculation of microorganisms, mainly from the families of *Thiobacillus*, *Thiomonas*, *Paracoccus*, *Acidithiobacillus*, *Sulfurimonas* or *Halothiobacillus*, which oxidize H_2S to elemental sulfur, sulfate, or thiosulfate through bacterial activity [9,16,23]. Biological-based methods have some advantages over the physical-chemical techniques, such as less intensive operational conditions, and thus, lower operational costs, energy consumption, and emissions of secondary pollutants [24,25]. Biological-based techniques can be divided into two categories: internal

and external desulfurization [20]. An internal desulfurization system applies microaerobic conditions directly into the anaerobic digester headspace. External desulfurization includes bioscrubbers, biotrickling filters (BTF), biofiltration, and external microaeration, where the micro-aerated environment is separate from the digestion environment, with H_2S removal occurring in a separate biogas vessel between the digester and the biogas utilization equipment [26].

According to Wu et al. (2020), BTF is currently the most widely used method for cost-effective H_2S removal [25]. It has been suggested that the biological process should be monitored and controlled to reduce issues, such as bed clogging [27]. Additionally, with high H_2S concentrations in the biogas, a nitrate source may be needed to support high biological growth rates [24,25]. Using a BTF system, Zhang et al. (2020) obtained more than 95% H_2S removal, and Dupnock and Deshusses (2020) showed more than 97% H_2S removal from biogas [10,12]. Wu et al. (2020) showed 100% removal of H_2S using a slightly alkaline BTF with polypropylene rings as the packing material and air injection to provide the O_2 used as the electron acceptor [25]. Khanongnuch et al. (2019a, 2019b) used *Thiobacillus* sp. as a sulfur-oxidizing and nitrate-reducing bacterium in a BTF to achieve >99% H_2S removal from a gas stream while simultaneously removing NO_3- [28,29].

While biofiltration is less common than BTF, biofiltration has also been shown to be effective for H_2S removal [27]. A biogas upgrading system based on the microalgae *Chlorella sorokiniana* provided 100% H_2S removal, with oxidation of H_2S to sulfate [30]. Haosagul et al. (2020) showed 100% H_2S removal using a bioscrubber with *Pseudomonas*, *Leucobacter*, *Thioalkalimicrobium*, and *Brevundimonas* present [31]. Enrichment of SOB inoculum using Na_2S has been shown to increase H_2S removal by stabilizing and increasing the pH. Cheng et al. (2018) found a stable H_2S removal, up to 95%, when a pH of 7.5 to 8.2 was maintained in the sludge [32].

Microaeration consists of dosing very small amounts of oxygen into an anaerobic digester, converting H_2S to elemental sulfur, sulfate or thiosulfate [33]. Microaeration has shown a great potential for H_2S removal due to lower costs, yet there are still challenges that need to be addressed, such as the need for periodic maintenance to avoid clogging problems in the microaeration pump, and the contamination with N_2 with air injection [34]. Large-scale digesters have shown from 80 to 100% H_2S reduction using microaeration [6].

Alternative H_2S reduction methods have also been investigated. Adding gummy vitamin waste to dairy manure digesters reduced the H_2S content in the biogas by 66 to 83% [7]. Waste-derived adsorbent materials (wood-derived biochar, sludge-derived activated carbon, and activated ash) were used for H_2S removal, with the activated ash having the highest H_2S removal efficiency (3.2 mg H_2S/g of adsorption capacity) and the sludge-derived activated carbon having the lowest efficiency (2.2 mg H_2S/g of adsorption capacity) [35]. While biochar impregnated with Fe had 100% H_2S reduction in diary manure digesters, and unmodified biochar resulted in 90.5% H_2S removal [20].

Farmers in rural Latin America operate over 1100 small-scale agricultural digesters compared to over 350 in the US and over 1100 in Europe [36,37]. Many small farmers in Latin America use digesters to manage their manure. In Peru, the most common technique to remove H_2S is filtration using iron chips or iron sponges, which is used in ecological education centers, such as Casa Blanca in Pachacamac, Peru. Microaeration has been applied mainly in large-scale digesters. Most small farmers in Latin America have not used microaeration to remove H_2S from biogas and rely on iron filtration. This study aims to demonstrate how microaeration compares to iron filtration in terms of H_2S removal efficiency and cost for small-scale digesters. This research compared two low-cost techniques: traditional iron filters used in Latin America and microaeration in removing H_2S from biogas produced in a field-scale digester in Peru. The objectives of this research were to (1) test the efficiency of duplicate microaeration vessels using two retention times to reduce H_2S from biogas, (2) compare the efficiency of microaeration to the use of iron filters in duplicate, and (3) conduct a cost analysis based on the quantity of H_2S removed. The results can be used to understand how efficiency, cost, and accessibility affect H_2S removal techniques used by thousands of small-scale anaerobic digester operators.

2. Materials and Methods

2.1. Digestion Reactor

A field-scale digestion system using the Taiwanese-model was constructed using high density polyethylene (HDPE) at the Model Centre for Solid Waste Treatment (CEMTRAR) in La Molina, Lima, Perú. The reactor capacity was 8.5 m^3, with a 6.37 m^3 liquid volume and a 2.13 m^3 biogas headspace (Figure 1). The reactor was loaded daily with swine manure from the Porcine Experimental Unit at La Molina National Agrarian University (UNALM) in Lima, Peru, using an average organic loading rate of 1.13 kg VS/m^3 d. The manure had 31.6% total solids (TS), with 0.73% sulfur (S). During the study, the temperature and pH of the effluent were measured daily, with an average temperature of 21 ± 2 °C in the digester (ambient temperature conditions), an average pH of 7.44, and an average retention time of 50 days. Analyses of the liquid manure entering the digester were conducted by the UNALM Laboratory for the Analysis of Water, Soils, Plants and Fertilizers. These analyses included percentage of carbon, using the modified Walkley and Black method [38], oxidizing organic carbon with potassium dichromate, and percentage of nitrogen according to the Kjeldahl method [39]. The TS (total solids) and VS (volatile solids) of the swine manure were measured according to Standard Methods [40], and the pH using the electrometric procedure according to US EPA Method 9045D. The percentage of sulfur was measured using a turbidimetric method using barium chloride, and percentage of sodium using atomic absorption spectrophotometry, according to Method 3111 [41]. The digester had operated for seven years prior to this experiment, with no specific desulfurization method utilized during prior operation.

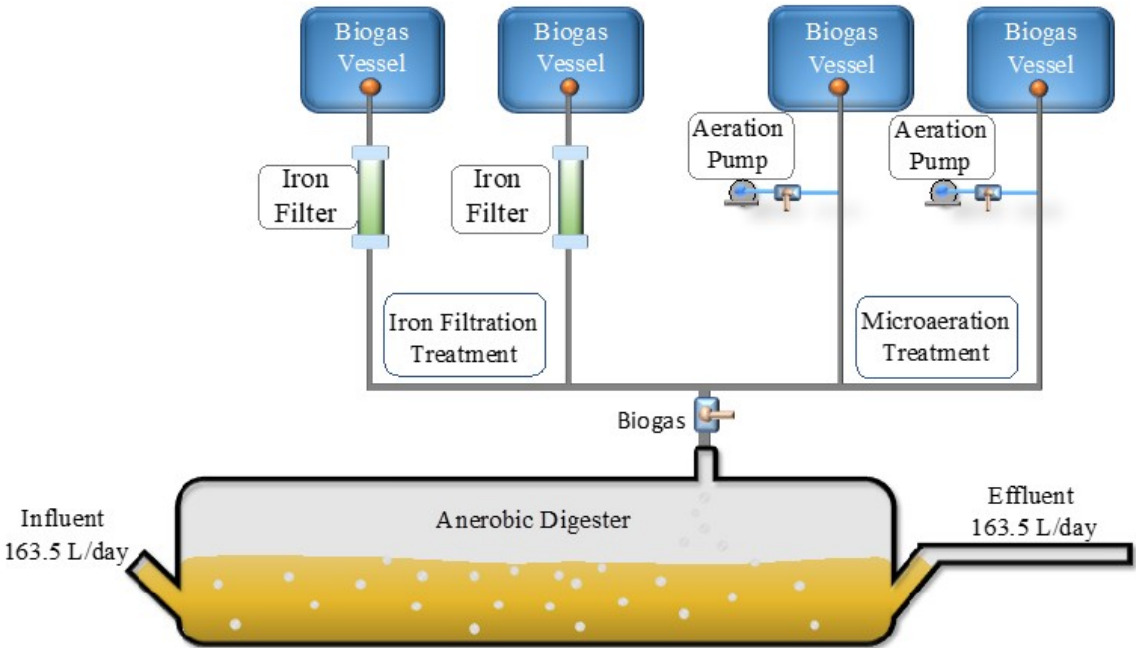

Figure 1. Schematic design of duplicate treatments for the desulfurization of biogas using iron filtration and microaeration.

Upon exiting the digester and before entering the biogas storage vessels, the untreated biogas was analyzed for CH_4, CO_2, O_2, H_2, and H_2S using a Multitec 545 gas analyzer (Sewerin, Gütersloh, Germany). The biogas was stored in four separate biogas vessels, with two vessels storing the biogas after duplicate microaeration injection, and two vessels storing the treated biogas after passing through the duplicate iron filters. The composition of the treated biogas in each vessel was analyzed daily using the Multitec 545 gas analyzer. The biogas production rate was measured with

a flowmeter (Pa 2-25l Flow Meter, Barry Century, Beijing, China) once a day while the digester was loaded with manure.

2.2. Micro-Aeration

Biogas microaeration was conducted using duplicate biogas vessels composed of a thick Low Density Polyethylene (LDPE) (0.208 m^3 each). The biogas holding vessels were loaded and unloaded daily to renew the biogas and simulate daily use of the biogas. After each vessel was loaded with biogas, ambient air was pumped into the headspace of the biogas vessels for approximately one minute using an air pump (Venus AP 208, Shanghai, China), with a minimum and maximum flow rate of 2 and 3 L/min, respectively. Approximately 2.08 L of air were injected daily (1% of the vessel volume). Measurements were taken daily at 2 and 4 h after the single air injection to test the effect of two retention times on the biological oxidation process.

Each microaeration vessel was inoculated with SOB using 10 L of sludge from the anaerobic digester outlet. This sludge was characterized after the end of the experiment for total S and sulfate. The microaeration treatment experiment began over three stages. Initially, microaeration tests were conducted before inoculum introduction. Inoculum was then introduced and a start-up period of 3 days was given for adaption before the microaeration treatment began. The monitoring period was 50 days from 28 June to 16 August 2018.

2.3. Sulfur-Oxidizing Bacteria (SOB) Observation and Isolation

The SOB observation and isolation technique was based on the methodology from the Open and Distance National University [42] in Bogotá, Colombia. The H_2S-oxidizing microorganisms were grown using 1 mL of sludge from each microaeration vessel inoculated separately in tubes consisting of an incubated culture medium at 37 °C. The criteria for identifying SOB-positive tubes were (1) visualization of the turbidity of the medium, (2) microscopic verification of the growth of the microorganism in the medium liquid using an optical microscope, and (3) observation of the presence of colonies in the solids. Due to the high bacterial density in the tubes, isolates were taken and incubated in a solid medium to obtain pure cultures. Finally, a Gram stain was used to identify the phenotypic characteristics of the isolated SOB colonies in the digester effluent samples and replicate microaeration vessels using a 100x microscope with a stereoscope.

2.4. Iron Filter

Two 0.979 L iron filters were built using two PVC tubes (0.1108 m × 0.1016 m) filled with iron sponge (domestic material used for scrubbing pots and pans), which was composed of iron oxide (Fe_2O_3). Prior to use, the iron sponge substrate was immersed in HCl and NaOH solutions to oxidize the material. The biogas from the digester passed through one of the two duplicate iron filters positioned inside a biogas conveyance hose. The scrubbed biogas then entered the connecting duplicate biogas vessels.

The filter substrate (iron sponge) was renewed every 10 days during the 50 day experiment. The quantity of the filter material needed for the total H_2S removal was based on the average of the biogas production rate (0.5 L/min) measured prior to the experiment and average H_2S concentration in the biogas (3000 ppm). The calculations were based on Equations (1) and (2) above and previous research that showed the H_2S absorption limit of iron sponge is 56% (0.56 kg H_2S/kg Fe_2O_3), resulting in 7.45 g of Fe_2O_3 needed for H_2S removal [5,43,44]. The amount of Fe filter used in each PVC pipe was 8.94 g Fe_2O_3, resulting in 20% more filter added than the theoretical need.

2.5. Statistical Methods

Statistical analysis, including ANOVA and multiple regression was performed using Minitab 18, with significance defined at alpha of 0.05. A non-parametric Kruskal–Wallis test using the percentage

removal of H_2S was performed, with the levels based on applied treatment technology (iron filter or microaeration) and retention time (2 or 4 h), as the samples were independent of each other.

3. Results and Discussion

3.1. Digester pH and Temperature and Initial H_2S Concentration

There was no significant correlation between the pH of the digester and the initial (pre-treatment) H_2S concentration in the biogas (p-value = 0.178). The digester pH started high (8.14) at the beginning of the 50 day experiment, with an average of 7.44 and a range of 6.91 to 8.33 over the 50 days, with 4 of 32 data points < 7. The pH values did not correspond with the H_2S concentration from the digester, which started low (2300 ppm H_2S), increased to a maximum of 4000 ppm, but remained <3500 ppm after Day 33 and <3000 ppm from Days 48–50. The variation in the H_2S concentration was more likely influenced by the influent S concentration and bacterial community than the pH value in the digester. According to Krayzelova et al. (2015), the concentration of H_2S can increase when the pH decreases [23], influencing the distribution of sulfur in the liquid and gas phases.

The temperature of the digester was kept in the lower portion of the mesophilic temperature range (15–35 °C), ranging from 17.8 to 29.9 °C during the 50 day experiment. There was no significant correlation between the temperature of the digester and the initial (pre-treatment) H_2S concentration in the biogas (p-value = 0.703). The digester and the biogas holding vessels were maintained at ambient temperature, with some fluctuations between day and night temperatures.

3.2. Biological Desulfurization Using Microaeration

Prior to inoculation of the biogas vessels with SOB, a microaeration environment was maintained through injecting ambient air into the empty biogas vessels, with a H_2S removal efficiency ranging from 29.4 to 72.1%, with an average of 55.2 ± 7.1%. Without the relevant bacteria in the inoculum, the sulfur could only be oxidized through reacting with the O_2 in the air. According to van der Zee et al. (2007), this process is not as efficient as bacterial oxidation [45].

The 10 L of sludge added for microaeration was based on the study of Ramos et al. (2013) [46], which suggested a volumetric ratio of 1:10 inoculum to desulfurization unit volume. During the three day inoculum stabilization period, the H_2S reduction efficiency increased from 59.8% on Day 2 to 74.9% on Day 3. By Day 4, 100% H_2S removal was achieved, indicating that a bacterial adjustment period of three days was needed for optimal removal efficiency. The replicate average of the H_2S removal 2 h after air injection was 91.5 ± 1.87%, increasing to 99.8 ± 0.04% after 4 h (Figure 2), with 4 h having a significantly higher H_2S removal efficiency than 2 h (p-value < 0.001). In five of the 50 days, efficiencies of 100% were achieved for 2 and 4 h. Adding up to 3% air in the microaeration reactor completely removed the H_2S content (around 4000 ppm) in the biogas for these five days. The H_2S removal efficiency was significantly affected by the initial H_2S concentration (p-value = 0.026). The duplicate microaeration treatments were not significantly different during the 50 day experiment (p-values = 0.995 for 2 h retention time and 0.308 for 4 h retention time).

Similar results were obtained by Ramos et al. (2013), with high removal efficiencies obtained at a maximum H_2S content of 0.35% v/v (3500 ppm) [46]. Krayzelova et al. (2015) also found residence time (RT) to be a key factor in microaeration, with efficiencies > 97% H_2S removal commonly achieved with a RT > 5 h [23]. According to Schneider et al. (2002), 88% H_2S removal efficiency was found with a residence time of 2.5 h, while it was less than 40% if the time was <1.25 h [47]. Ramos et al. (2014) had a 2.5 h RT [48], with 88% H_2S removal, and Köchermann et al. (2015) achieved 99% H_2S removal in 4.0–5.5 h [49]. Montalvo et al. (2020) demonstrated H_2S removal exceeding 90% in most cases with similar RTs (2.8–4.8 h), while maintaining flammable biogas concentrations [19].

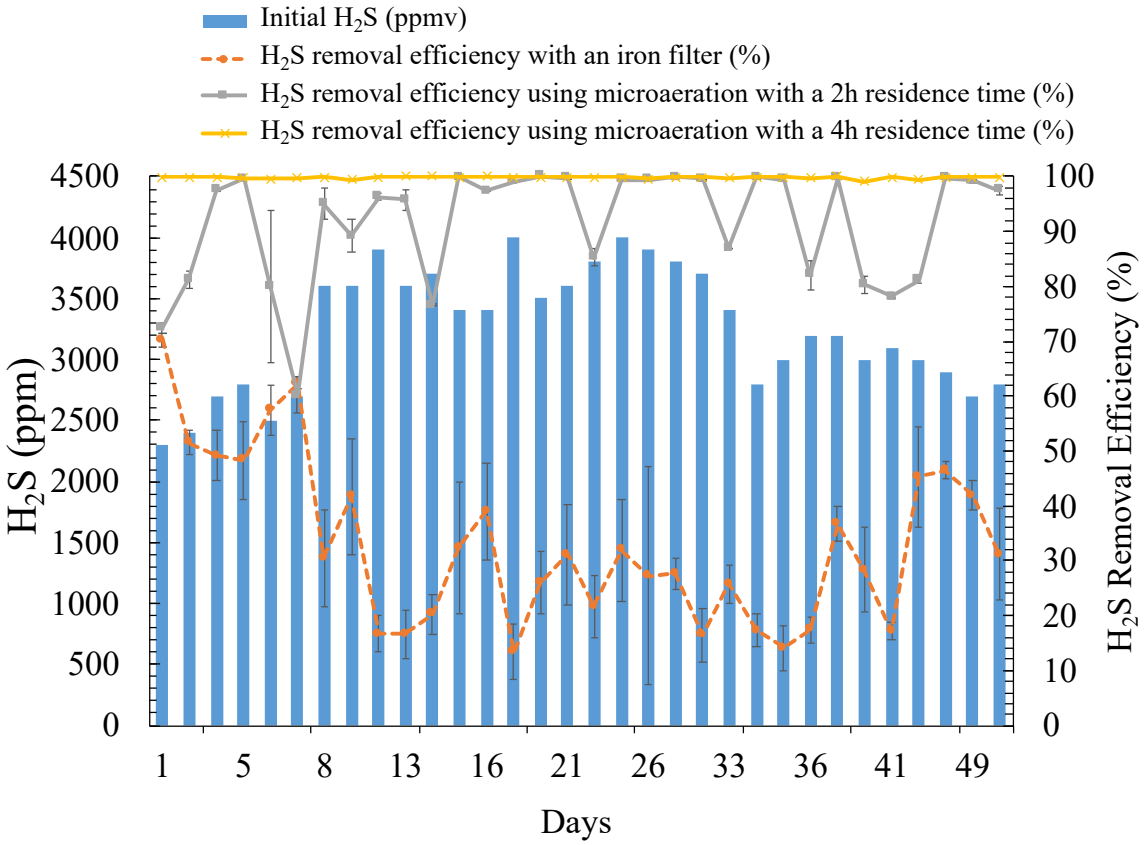

Figure 2. Relationship between initial H_2S (ppm) and H_2S removal efficiency (%) using iron filter and microaeration treatments, with gas analysis at 2 h and 4 h after initial air injection for microaeration.

The CH_4 and CO_2 concentrations in the microaeration vessels decreased with ambient air injection due to the presence of nitrogen gas (N_2) in ambient air diluting the biogas [27,33] (Figure 3). When there was 3% residual O_2 in the biogas after microaeration, more than 3000 ppm of H_2S was removed, indicating that the air injection was higher than the rate needed for H_2S removal. When the O_2 level was <3%, the CH_4 concentration values were not significantly different before and after microaeration (p-value = 0.58). When the O_2 concentration in the biogas after microaeration was >3%, the CH_4 was significantly lower after treatment (p-value = 0.004). The average CH_4 concentration prior to microaeration was 56.6%, which is equivalent to 22,555 kJ/m^3 of biogas. Two hours after microaeration, the average CH_4 concentration decreased to 53.8% (21,404 kJ/m^3 of biogas), decreasing to 52.8% CH_4 (20,982 kJ/m^3 of biogas) 4 h after microaeration. In Mulbry et al. (2017), there was no apparent trend between aeration and percentage of CH_4 with O_2 concentrations ≤ 1% [33]. Díaz et al. (2011) showed that the concentrations of CO_2 and CH_4 remained stable during microaeration with O_2 direct (not the air injection) [50]. According to Köchermann et al. (2015), lower O_2 concentrations would be expected at higher concentrations of H_2S [51]. Giordano et al. (2019) achieved nearly 100% H_2S reduction in a full-scale thermophilic digester using microaerobic conditions with residual oxygen ranging from 0.2 to 2.0% O_2 [52].

There was no significant relationship between the microaeration vessel temperature and H_2S removal efficiency (p-value = 0.323). Ramos et al. (2013) showed higher H_2S removal efficiencies with higher temperatures, concluding that temperature does affect the process [46]. According to de Arespacochaga et al. (2014), increasing the temperature from 10 to 30 °C increased H_2S removal efficiency, with the highest H_2S removal using the bacterial consortium at 35 °C [8]. However, in our field-based study, the reactor temperature was based on ambient air temperature, and thus it fluctuated throughout the day and across days, resulting in no clear relationship.

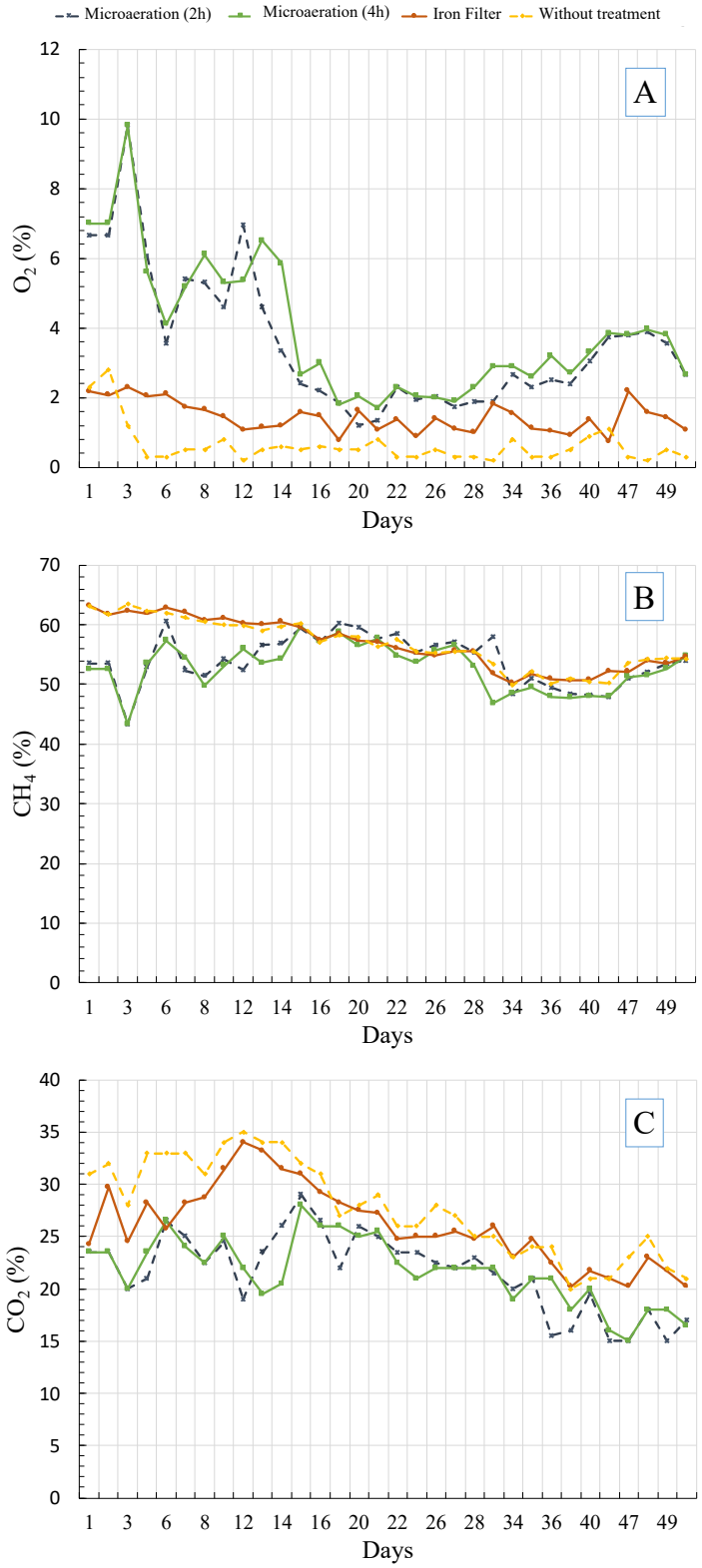

Figure 3. The concentrations of O_2 (**A**), CH_4 (**B**), and CO_2 (**C**) in the biogas over 50 days showing concentrations pre-treatment, with iron filter H_2S removal and microaeration.

Sulfide Oxidation during Microaeration

The microaeration inoculum source added to the biogas reactors had an initial elemental sulfur (S) concentration of 259 mg/L and a sulfate concentration of 771 mg/L. At the end of the

experiment, the microaeration biomass had an elemental sulfur concentration of 1536 mg/L, and a sulfate concentration of 4606 mg/L. The influent (164 L/day) contained 42,347 mg sulfur and 126,059 mg sulfate, while the effluent contained 251,136 mg sulfur and 753,081 mg sulfate (Figure 4), a 493% and 497% increase in concentration, respectively. The average daily H_2S removed was 4.52 mg/L after a 4 h retention, and 1.49 mg/L after the iron filter (Figure 4). At the end of the experiment, neither sulfate nor sulfur clusters were visualized, but the results showed a large increase in elemental sulfur and sulfate in the microaeration biomass, indicating that H_2S in the biogas was oxidized by SOB in greater amounts than the amount of sulfur that settled in the biomass.

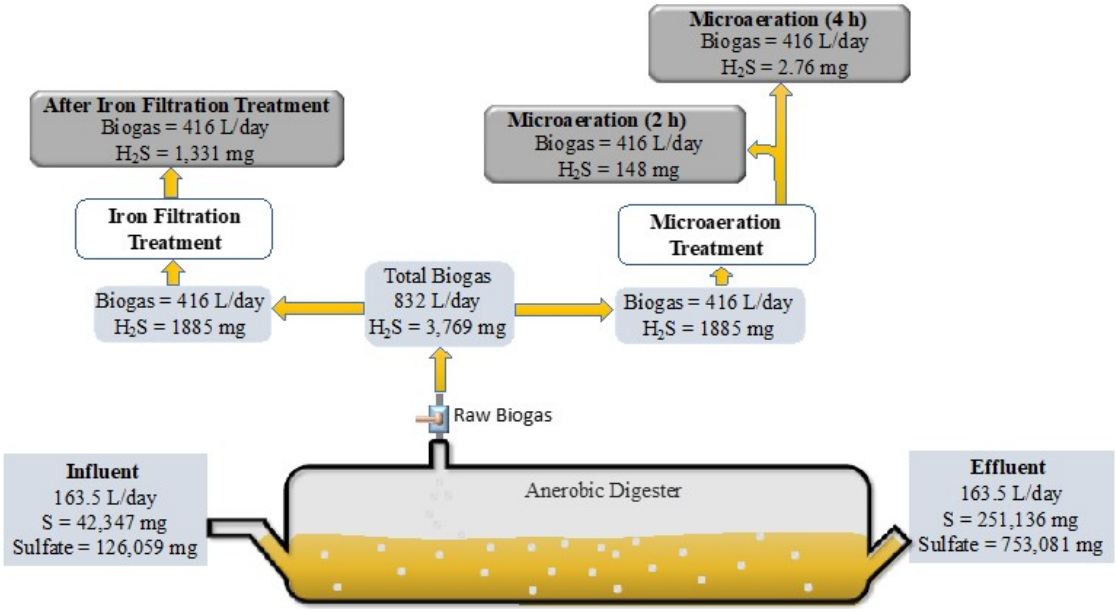

Figure 4. Schematic diagram of the sulfur mass balance.

Sulfide oxidation with O_2 during microaeration can form polysulfides (S^2-n), which are protonated to form elemental sulfur [45,53,54], and can then form more oxidized species of sulfur, such as thiosulfate, sulfate, and sulfite [45,54,55]. Ramos et al. (2013) observed precipitated sulfur in the sludge near the liquid surface. This observation was not seen in this study, possibly due to the length of time: 50 days in our study compared to their 91 day study [46]. Mahdy et al. (2020) showed slight sulfate accumulation (<330 mg L^{-1}) inside the microaerated digesters and higher sulfate concentrations in the effluents of microaerated digesters than in the control [56].

At the end of the study, the sludges from the digester and microaeration vessels were examined to enumerate and characterize the SOB bacteria. There were >11 × 10^4 MPN/g of bacteria in the fresh sludge added to each of the microaeration vessels. The bacteria in the microaeration biomass from one of the vessels included wavy-edged, creamy-surfaced, white-colored, and irregular-shaped bacteria, while the other vessel included whole-edged, creamy-surfaced, irregular-shaped, and translucent-colored bacteria. In one microaeration vessel, the bacteria average size was 0.85 mm and they were Gram-negative, with short and thick coccobacilli, characteristics that are consistent with *Thiobacillus sulfooxidans*. The second microaeration vessel had bacteria that were 2.73 mm and included short and thick coccobacilli, which could also have been in the *Thiobacillus* group, but this is not conclusive [42]. Hurtado and Salamanca (2017) analyzed the phenotypic characteristics of oxidizing strains of sulfur bacteria and described the characteristics as 5 mm diameter, long and thin bacilli and Gram-negative, which is generally consistent with the bacteria found in the digester effluent inside both microaeration vessels.

3.3. Desulfurization Using the Iron Filter System

The average H_2S removal efficiency using iron filters was 32.91%, with a maximum of 70.21% and a minimum of 13.39% (Figure 2). H_2S removal efficiency by iron filters was significantly lower than for microaeration (p-value < 0.001). While McKinsey (2003) indicated theoretical efficiencies of up to 85% (0.56 kg H_2S/kg Fe_2O_3) in batch mode, the maximum H_2S removal efficiency was reached on the first day of this experiment, with significant reductions in H_2S removal efficiency over time (p-value < 0.001) [44]. The H_2S efficiency was significantly affected by the pre-treatment H_2S concentration (p-value = 0.026), with decreases in removal efficiency with higher pre-scrubber H_2S concentration. Figueroa (2019) [57] stated that an iron filter can remove approximately 50% of H_2S and is the most common method utilized in countries like Peru, where small-scale digesters are prevalent. Neither CH_4 nor CO_2 were affected by the iron filter, with no significant differences between CH_4 (p-value = 0.119) and CO_2 (p-value = 0.986) concentrations before and after iron filter treatment. In addition, no relationship was determined between the temperature of the digester and the H_2S removal efficiency when using the iron filter (p-value = 0.301).

3.4. Economic Analysis of Low-Cost H_2S Removal Technologies

Operational costs, infrastructure costs (packing material, equipment, pumps, iron filters, and piping), energy costs, and maintenance costs were evaluated. The energy cost to run the microaeration pump was \$0.26/year for microaeration with an air retention time of 4 h based on \$0.07kWh^{-1} (ENEL Peruvian company website). There were no energy costs for the iron filters. The construction and material cost for iron filters (\$31.0/year) was higher than for microaeration (\$6.5/year). After 4 h, microaeration removed 0.25 m^3 H_2S/year, which was much more efficient than using iron filters (0.06 m^3 H_2S removed/year). The operational costs were \$27/m^3 H_2S removed/year for 4 h microaeration and \$382/m^3 H_2S removed/year for iron filters. The operational cost of iron filters was higher due to adding new iron material 36 times/year due to the material wear, lost efficiency, and oxidation.

Iron shavings or sponges can be periodically regenerated by exposing the chips to 8% O_2, but this process is highly exothermic and should be carefully monitored [58]. Moreover, it has been shown that the regeneration efficiency decreases each time, with substrate replacement needed once saturation occurs [58]. In addition, each time the substrate is discarded and replaced, waste is generated, which must be disposed of properly. Moreover, a higher biogas generation rate will have a higher material cost and disposal cost due to higher replacement needs [58]. The microaeration technique has several advantages over iron filters, including simplicity, cost, and achieving an efficiency of up to 100%. In addition, it does not generate toxic waste nor are chemical reagents needed to use this technique. Microaeration can be conducted directly inside the anaerobic reactor or in a separate reactor. With either method, elemental sulfur can be produced and deposited on the walls of the digester or microaeration reactor. These sulfur deposits may need to be removed, if built up over time, but can be used as a fertilizer. Reduction in the percentage of CH_4 in the biogas does occur due to the N_2 dilution with air injection [59].

A previous study [60] reported a cost of \$0.015/m^3 biogas for biological treatment using an industrial-scale biotrickling filter, and \$0.027/m^3 biogas with $FeCl_3$ chemical oxidation treatment, which are both lower than our study (\$0.09/m^3 biogas for microaeration and \$0.41/m^3 biogas for iron filter) using small-scale systems [61,62]. Active carbon use had higher costs (\$0.13/m^3 biogas) for removing H_2S [10]. Microaeration appears to be cost competitive compared to market available, large-scale, H_2S removal technologies for use in small-scale systems in countries such as Peru, and was shown to be more efficient than using iron filters.

4. Conclusions

The introduction of small amounts of ambient air (1–3%) into biogas storage allowed for the removal of more than 3000 ppm H_2S daily from the produced biogas, often reaching a H_2S concentration

lower than the detection level (1 ppm). Microaeration H_2S removal also remained stable during the 50 day experiment, while the iron filter treatment efficiency decreased over time. Efficiencies of 100% H_2S removal were achieved with the microaeration method, while a maximum efficiency of only 70.2% was obtained with the iron filter system, decreasing to 13.4% H_2S removal efficiency after 50 days. The costs for the desulfurization process using the iron filter system ($382/m^3 H_2S removed) in small-scale digesters in Peru were higher than for the microaeration method ($27/m^3 H_2S removed), yet most small-scale digester operators continue to use iron filter systems in Peru. This study should help illustrate the quantifiable benefits of microaeration for H_2S removal compared to iron filters.

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