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Desulfurization of Biogas from a Closed Landfill under Acidic Conditions Deploying an Iron-Redox Biological Process

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Abstract: Desulfurization processes play an important role in the use of biogas in the emerging market of renewable energy. In this study, an iron-redox biological process was evaluated at bench scale and pilot scale to remove hydrogen sulfide (H_2S) from biogas. The pilot scale system performance was assessed with real biogas emitted from a closed landfill to determine the desulfurization capacity under outdoor conditions. The system consisted of an Absorption Bubble Column (ABC) and a Biotrickling Filter (BTF) with useful volumes of 3 L and 47 L, respectively. An acidophilic mineral-oxidizing bacterial consortium immobilized in polyurethane foam was utilized to regenerate Fe(III) ion, which in turn accomplished the continuous H_2S removal from inlet biogas. The H_2S removal efficiencies were higher than 99.5% when H_2S inlet concentrations were 120–250 ppmv, yielding a treated biogas with H_2S < 2 ppmv. The ferrous iron oxidation rate (0.31 $g \cdot L^{-1} \cdot h^{-1}$) attained when the system was operating in natural air convection mode showed that the BTF can operate without pumping air. A brief analysis of the system and the economic aspects are briefly analyzed.

1. Introduction

The use of biogas from municipal landfills to obtain energy (electricity generation) is a growing trend worldwide as part of the quest for clean energy alternatives to the traditional fossil fuels [1]. Landfill biogas is produced by the anaerobic digestion of organic wastes, and its composition depends on the type and age of digested organic matter. Typically, landfill biogas is composed of methane (CH_4) 50% v, carbon dioxide (CO_2) 45% v, alkanes/alkenes (C_7H_8–$C_{16}H_{34}$) 0.1–85.3 mg·m^{-3}, chlorides (CCl_4–C_2HCl_3) 0.14–4.52 mg·m^{-3}, mercury compounds (CH_3Hg–$(CH_3)2Hg$) 1–91 μg m^{-3}, siloxanes 1–17 mg·m^{-3}, volatile organic compounds (VOCs) (benzenes, isopropyl benzene, halogenated compounds) 5–85 mg·m^{-3} and hydrogen sulfide 0.005–2% v [2]. The H_2S content depends on the composition and age of the waste disposed in the landfill besides the protein content in organic waste [3,4].

Hydrogen sulfide must be removed from biogas due to technical problems related to corrosion in pipes, pumps, engines, gas storage tanks and electric power plants, as well as the fact of it being

a potential pollutant when it is combusted, producing sulfur dioxide (SO_2) [3]. This gas is further oxidized, which promotes acid rain containing sulfuric acid (H_2SO_4) [5]. Additionally, it causes a bad odor at very low concentrations due to its low odor threshold (1 ppbv) [6].

The final use of biogas, composition and flow variability, concentration of H_2S, and the absolute quantity of H_2S to be removed define the requirements of the desulfurization technique to be deployed [4]. To remove the H_2S content in a biogas stream, there are several physicochemical technologies with good removal efficiencies (> 99%) [3]. LO-CAT® technology is an example of a physicochemical technology that has been applied in more than 120 plants around the world [7]. The removal mechanism is based on a series of chemical reactions of H_2S with iron chelating agents under slightly alkaline conditions [8,9]. The products, after the chemical H_2S removal, are elemental sulfur and ferrous ion, the former being recovered by sedimentation, while ferrous ion is continuously oxidized into ferric ion using an inlet air stream [7]. Moreover, under acid conditions (pH < 2) the chemical H_2S reactions with ferric ions can be carried out without chelating agents because iron (both Fe(II) and Fe(III)) remain soluble without sulfide iron precipitation; however, under acidic conditions, the oxidation rate of ferrous ion by molecular oxygen is slow [7]. Certain bacteria, such as *Acidithiobacillus ferrooxidans,* play an important role in increasing the rate of ferrous iron oxidation into ferric iron. Meruane and Vargas [10] showed that at a low pH (pH < 5), the rate of bacterial oxidation of ferrous iron is about 10^4 times larger than the corresponding rate of chemical oxidation. This result indicates that acidophilic iron-oxidizing bacteria, such as *A. ferrooxidans,* are a promising microorganism for usage in desulfurization processes, regenerating Fe(III) biologically [7]. In combination with physicochemical oxidation, *A. ferrooxidans* can act as catalyst of reoxidation of ferrous ions to achieve the removal of H_2S from biogas with lower operational and environmental costs compared with a sole physicochemical technology [9]. Nowadays, biological desulfurization treatments have gained attention due to the achieved removal efficiencies (> 99%) and are competitive with physicochemical methods. Some documented examples of biodesulfurization processes, including biological ferric ion regeneration, are biofilters, biotrickling filters, Biogas Cleaner®, Biopuric®, DMT filter®, LO-CAT® and SulFerox® among others [4,7,11–13]. However, challenges remain in the scaling up of these technologies in terms of the consumption of chelated iron, pH control, and overall economic balance of the process [14].

The aim of this work was to present the experimental performance of an on-site chemical-biological desulfurization system removing H_2S from biogas generated at a closed landfill. The effects of no pH control and no forced convection of air on the iron oxidation rates and H_2S removal were evaluated.

## 2. Materials and Methods

2.1. Microorganisms

An enriched acidophilic mineral-oxidizing bacterial consortium (AMOB), obtained from the sediments and soil of an acid mine drainage in Taxco Guerrero Mexico, was used as inoculum for the biological oxidation of the ferric ion. The AMOB was grown in medium 9K [15] containing ($g \cdot L^{-1}$): 3.0 $(NH_4)_2 SO_4$, 0.5 $MgSO_4 \cdot 7H_2O$, 0.5 K_2HPO_4, 0.1 KCl, 0.01 $Ca(NO_3)_2$ and 44.8 $FeSO_4 \cdot 7H_2O$ (corresponding to 9.9 g Fe(II) L^{-1}); the pH was adjusted to 1.6 with H_2SO_4.

2.2. Prototype Experimental System

The prototype system was previously tested in lab conditions, feeding controlled H_2S concentrations in defined air flow rates, which were made by mixing fresh air with a controlled flow of pure H_2S. Further details can be found elsewhere [9].

Figure 1 shows the prototype system installed in the closed landfill "Prados de la Montaña" in the western part of Mexico City. The landfill was closed in 1992; however, it continues to produce biogas, and further details can be found elsewhere [16]. The prototype system was connected to a venting-outlet of the landfill through a peristatic pump that supplied the sour gas at a flow of

960 L·d^{-1}. The prototype experimental system called Hybrid System at Pilot Scale (HSPS) consisted of two columns: an absorption bubble column (ABC) and a biotrickling filter (BTF) with useful volumes of 3 L and 47 L, respectively, and interconnected by a recycled aqueous stream. The 960 L·d^{-1} of sour biogas were fed at the bottom of the ABC co-currently with a 777 L·d^{-1} stream of 9K medium coming from the bottom of the BTF. The desulfurized biogas stream obtained from the top of the ABC was captured for a posterior composition analysis. The BTF was packed with polyurethane foam (EDT, Germany) with a specific area of 600 m^2·m^{-3}, a density of 35 kg·m^{-3} and a porosity of 0.97. The BTF was inoculated with the aforementioned AMOB. To keep aerobic conditions in the BTF, either a forced or a natural convective flow of air was implemented by pumping air at a flow of 82,000 L·d^{-1} to the BTF or just by keeping two air vents at extreme opposed sides of the BTF open, respectively. The forced and natural convective airflow tests allowed for the evaluation of the re oxidizing rates of ferrous ions with a minimum input of energy for aeration. The 9K medium was trickled from the top of the BTF with a flow of 3740 L·d^{-1}. The pH was maintained at 1.2 without an automatic control, and the temperature oscillated between 5 and 30 °C due to the outdoor conditions prevailing in Mexico City. The water evaporation was compensated daily with fresh water, while the 9K medium was renewed every 3 months. The HSPS was operated continuously for around 7 months.
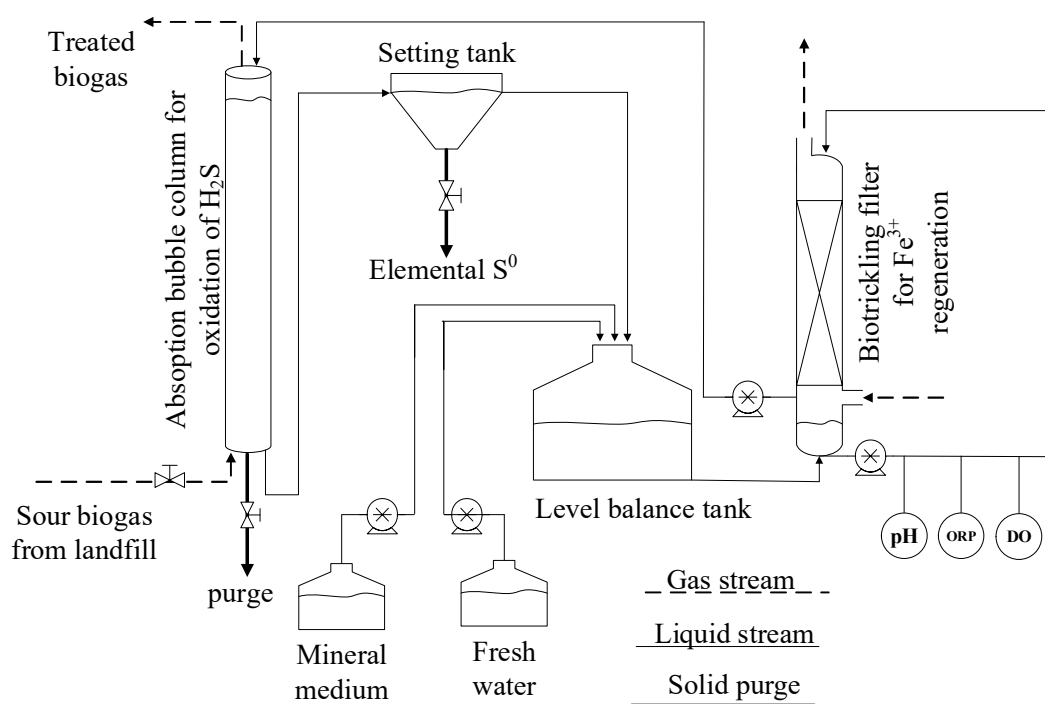
Figure 1. Desulfurization Hybrid System at Pilot Scale (HSPS) installed on a landfill cover.

The Fe(III) ion regeneration rate in the BTF was evaluated under a batch operation, with an initial Fe(II) concentration of around 4.5 L·d^{-1} under the continuous recycling of the 9K aqueous medium at the conditions described above.

The predominance zones diagrams for the stable iron and sulfur species with water under the experimental conditions were calculated with the software HSC Chemistry® Version 4.1 (Outokumpu Research Oy, Pori, Finland). The software computes the predominance zones in the pH vs. Oxidation-Reduction Potential (ORP) graph (also called Pourbaix diagram) at equilibrium. The software inputs are the total molal sulfur and iron concentrations in the aqueous phase contained in the HSPS, as well as the system conditions (temperature and pressure).

2.3. Analytical Methods

　　During the operation of the desulfurization system, the gas phase H_2S concentrations were continuously measured using an Odalog sensor with a range of 1–1000 ppm (App-Tek, distributed by Detection Instruments, Phoenix, AZ), which included a temperature sensor. In the aqueous phase, the total iron concentration in the 9K recycling medium was measured by titration with potassium dichromate and barium diphenylamine-sulfonate according to the method reported by Vogel [17]. Samples were collected from the bottom of the BTF and in the ABC. The ORP was measured with a polished platinum probe, using an Ag/AgCl electrode as a reference (EW-27018-40, Cole Parmer, Vernon Hills, IL, USA). The dissolved oxygen (DO) was monitored through a polarographic probe (Hanna Instruments, Woonsocket, RI, USA), and both ORP and DO were recorded online by means of a personal computer.

3. Results and Discussion

*3.1. Oxidation of Ferrous Iron in the BTF*

　　Figure 2A shows the depletion of Fe(II) in the culture medium under continuous forced air supply to the BTF. In this experiment, the Fe(II) oxidation rate was around 8.16 g·L^{-1}·d^{-1}, which, compared with the value of 0.19 g·L^{-1}·h^{-1} reported by Daoud and Karamanev [18], it shows that ferrous iron-oxidizing bacteria consortia used in our study have an adequate response to the reactor fixed conditions (pH, nutrients, airstream, flow recirculation, etc.). Moreover, Figure 2B shows that Fe(II) oxidation in the BTF was effective both under air forced convection (initial 250 min of experiment) and under the natural convection mode (final 130 min). The ferrous iron oxidation rate was calculated as 7.44 g·L^{-1}·d^{-1} in the natural convection mode, being similar to the rate obtained with the forced air convection (9.12 g·L^{-1}·d^{-1}). These results suggested that the BTF can operate under a natural convection mode to accomplish the biological oxidation of Fe(II). The dissolved oxygen concentration in the trickling liquid remained constant around 0.0065 g·L^{-1} for both assays, confirming that for this BTF the oxygen mass transfer did not limit the Fe(II) biological oxidation.
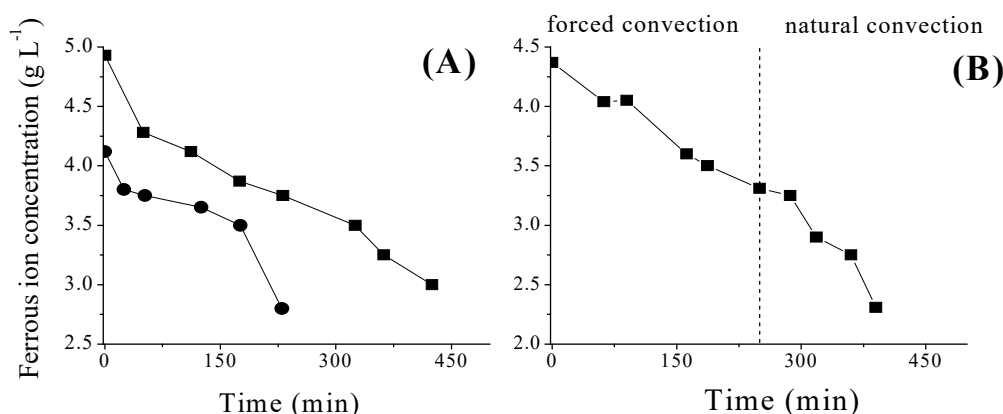
Figure 2. Biological oxidation of Fe(II) to Fe(III) in (**A**) the forced convection mode (black squares: assay 1, black circles: assay 2) and (**B**) the forced/natural convection mode (black squares: mixed assay).

*3.2. Removal of H_2S in the Prototype Hybrid System under Lab Conditions*

　　During the lab assays, Figure 3A,B show the results of the H_2S elimination capacity at inlet concentrations of 500 and 1000 ppmv respectively fed to the prototype hybrid system operated at the natural air convection mode for 120 h.
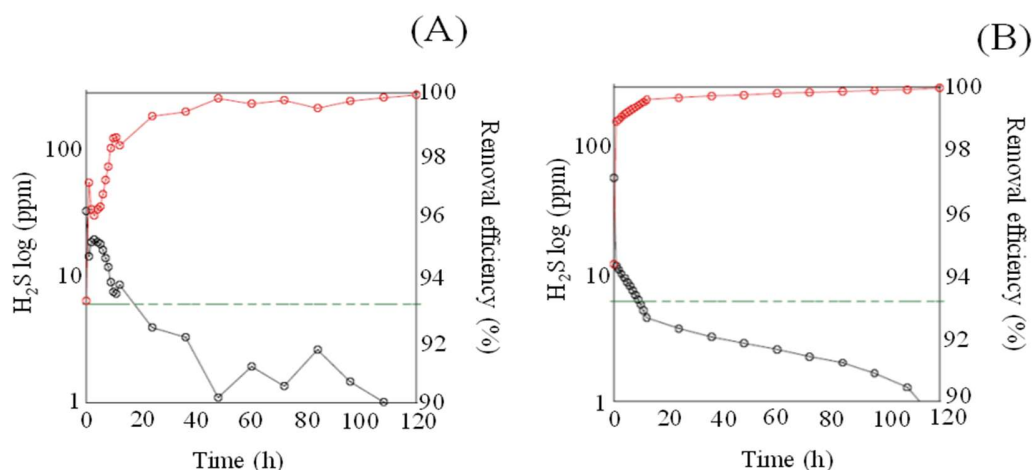
Figure 3. The removal efficiency of H_2S at inlet concentrations of (**A**) 500 ppmv and (**B**) 1000 ppmv. Red circles: % removal efficiency; black circles: outlet H_2S concentration.

The results show that the outlet gaseous H_2S concentrations decrease through time and that this is sustained due to the continuous chemical reaction of H_2S with Fe(III) and the subsequent biological oxidation of Fe(II) into Fe(III). After the first 20 h, the average elimination capacity of H_2S was 99% for both 500 and 1000 ppmv of H_2S. Ho et al. [19] reported H_2S removal efficiencies of around 82% under similar gaseous residence times (4 min), from inlet H_2S concentrations of 1500 ppmv using ferric iron concentration between 9 and 11 $g \cdot L^{-1}$. These authors report that *A. ferrooxidans* CP9 registered a high iron tolerance, up to 20 $g \cdot L^{-1}$. In our study, the pH between 1.6 to 2.0 at all times indicated conditions where the ferric ion precipitation is minimized [7], allowing iron ions to be continuously recycled to react with H_2S in the ABC and with O_2 in the BTF.

In our study, an average Fe(II) oxidation of 7.44 $g \cdot L^{-1} \cdot d^{-1}$ was estimated, showing that the biological system provided a sufficient ferric iron regeneration for the stable and efficient H_2S elimination from landfill gas. In comparison, recent reports show Fe(II) oxidation rates of 2.0 $g \cdot L^{-1} \cdot d^{-1}$ and 7.2 $g \cdot L^{-1} \cdot d^{-1}$ in batch and 161 $g \cdot L^{-1} \cdot d^{-1}$ in continuous systems [11–13]. This data was important for establishing the optimal operating parameters to scale up the hybrid system. Regarding the distribution of the iron species, a Pourbaix diagram of the system sulfur-iron-water was computed. This diagram considered the total iron concentration in the aqueous phase of the prototype system (4.5 $g \cdot L^{-1}$, 8.00×10^{-2} M) and the maximum dissolved sulfur concentration (2.17×10^{-5} M), estimated from both the H_2S aqueous solubility and average concentration close to 200 ppmv in the closed landfill vent, at an average temperature of 30 °C. The predominance zones diagram is shown in Figure 4. It can be seen that, theoretically, the Fe(III) ion is stable at a very narrow zone delimited by very specific conditions of ORP above +0.55 V and a pH below 0.5. However, when H_2S is absorbed in an aqueous solution at an acidic pH below 4.5, it reacts with $2FeOH^{2+}$, producing elemental sulfur (S^0), $2Fe^{2+}$ and water, as was recently described [20–22]. In our study, it is likely that this mechanism predominates under the conditions of our experimentation. This metastable zone is marked with a red circle on Figure 4. In our process, uncontrolled pH showed an average value of 1.8, while the mean ORP value was close to +0.5 V. Other studies reported that the optimum absorption rate of H_2S in ferric iron solutions occurs at pH 2.2 and that the absorption rate at pH 1.6 is expected to be approximately 50% lower [23]. In spite of this, we demonstrated satisfactory absorption H_2S rates with no need of extra equipment and reactants for the pH control.
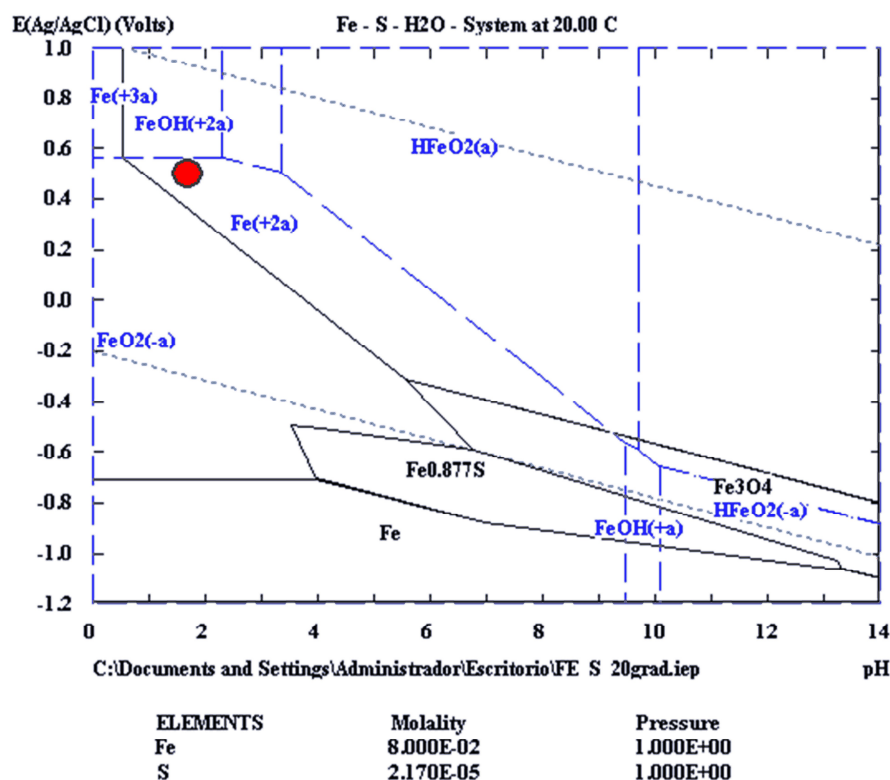
Figure 4. Predominance diagram zones at a total iron concentration of 8.00×10^{-2} M, total sulfur concentration of 2.17×10^{-5} M, and total pressure of 1 atm.

3.3. Performance of the Hybrid System at Pilot Scale (HSPS) in the Landfill

Figure 5 shows the inlet H_2S concentration and removal efficiency obtained during 50 d of operation of the HSPS installed in the closed landfill, where biogas contained a H_2S concentration between 120 to 250 ppmv. The results showed that the HSPS achieved an H_2S removal of up to 99.5% during the 50 d of sour biogas feeding. This removal efficiency guaranteed that H_2S in the treated biogas was below 2 ppmv. The pH and ORP values of the solution remained relatively constant around 2.0 and +0.5 V, respectively, as it was measured continuously during one week (see Figure 6B). In addition, no negative effect was registered on the biological process due to the exposition to outdoor conditions prevailing in the landfill, i.e., a diurnal temperature variation of 15 and 30 °C during the period of evaluation. The high H_2S removal efficiencies registered by the HSPS in the landfill were expected, as the concentration of H_2S in the sour biogas coming from the landfill and assayed during the lab evaluation stage never exceeded 500 ppmv, as shown in Figure 2A. De La Rosa et al. [24] mentioned that the biogas produced in this site contained small amounts of N_2, O_2, NH_3, H_2, CO, and traces of toxic substances (VOCs, mercaptans, gaseous mercury). In this respect, Zhang et al. [25] indicated that iron-oxidizing bacteria such as *A. ferrooxidans* can tolerate diverse organic compounds and metal ions within a certain concentration, which permitted survival and growth in extreme environments such as metal mines, coal mines, and sewage treatment plants. The good performance of the pilot plant in the landfill, registered during the on-site evaluation, showed the robustness of the combination of chemical and biological processes under the operational conditions here described. It is important to mention that the HSPS required minimum operational services, i.e., no aeration (natural convection) nor any pH or temperature control.
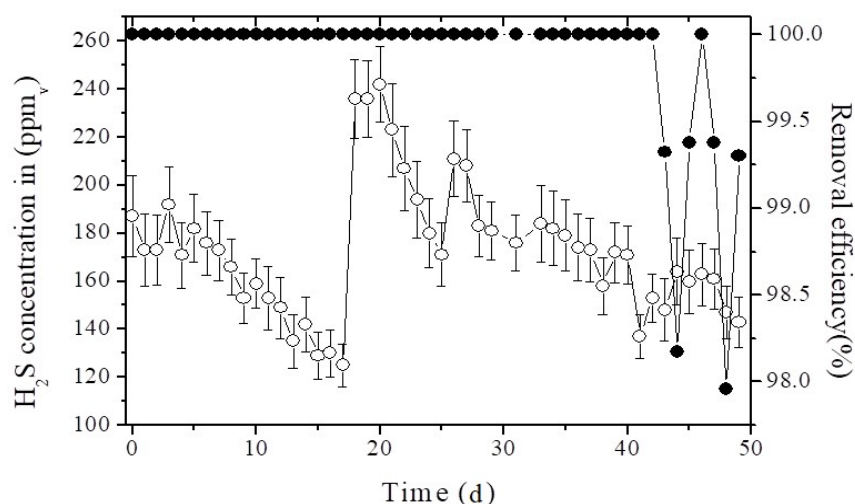
Figure 5. Performance of the HSPS in the landfill. H_2S inlet (○) and removal efficiency (●).

The inlet concentration of H_2S and the profile of the temperature of the biogas fed to the HSPS during the first week (Figure 6) showed that periodic variation of both parameters occurred through time. In addition, Figure 6 shows a decrease in the H_2S concentration in the biogas coming from the landfill, especially during the rainy season, probably due to the increment of moisture inside the landfill, which may cause a disequilibrium of the H_2S partition between gas and liquid in the landfill. However, these environmental factors do not affect the efficiency of the hybrid system, in particular the temperature variation, which can cause a negative effect on the biological activity.
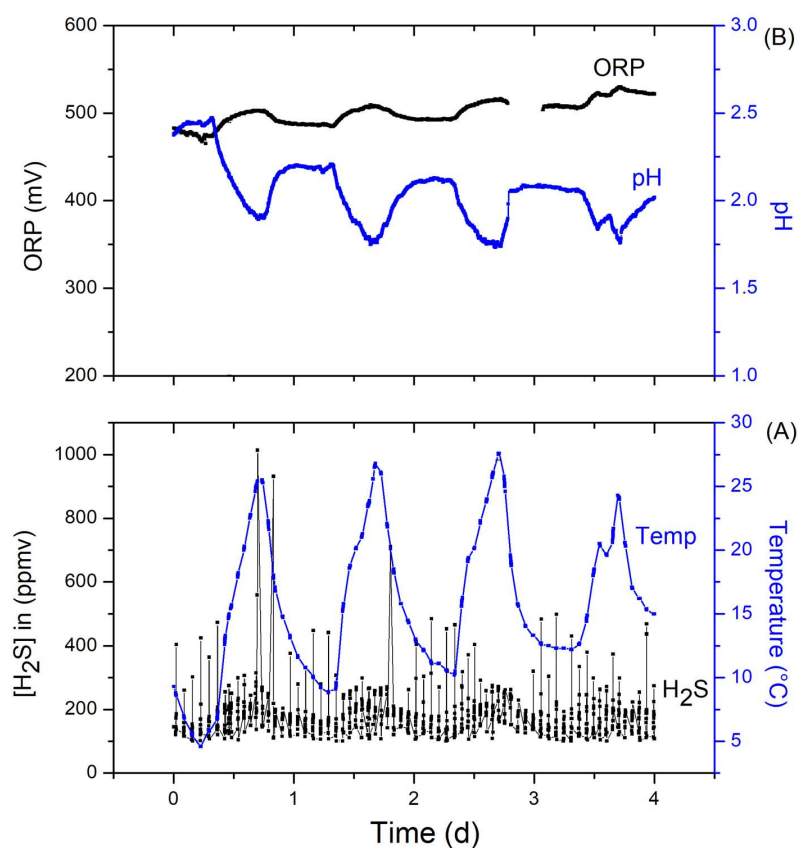
Figure 6. (**A**) The inlet concentration of H_2S and temperature profile; (**B**) the pH and Oxidation-Reduction Potential (ORP) profile of the aqueous solution in the HSPS, during the first week of November 2011.

Sulfate concentrations of around $10 \text{ g} \cdot \text{L}^{-1}$ were detected after one month of continuous operation of the HSPS on the landfill, probably as a result of the ability of these bacteria to oxidize sulfide species [6] to obtain energy. We did not recover any elemental sulfur in the settler due to its colloidal property, so the produced elemental sulfur accumulated in the BTF. This characteristic might signify an important advantage for the system in removing an excessive accumulation of elemental sulfur in the packed bed of the BTF, where a temporal interruption of the feeding of sour biogas can promote the consumption of this solid sulfur.

The HSPS operation under the aforementioned conditions needed 0.472 kW for its operation, corresponding mainly to the pumps consumption. However, the energy generation by burning $960 \text{ L} \cdot \text{d}^{-1}$ of biogas was calculated at 0.181 kW (considering a calorific value of 4.5 kWh per m^3 of treated biogas). This energetic analysis would indicate that under the present operational conditions the implementation of this technology is not energetically feasible using grid electricity to supply the system. Moreover, this analysis indicates that this biogas purification process would start to be energetically feasible when treating biogas flows greater than $2400 \text{ L} \cdot \text{d}^{-1}$. In this scenario, the implementation of alternative energy sources such as solar and wind would allow to make this energetic balance positive. Besides, the desulfurization of biogas remains important, keeping in mind that reducing methane emissions to the atmosphere might be accomplished by the combustion of desulfurized biogas, which can further aid the combustion equipment lifespan while also producing clean energy.

4. Conclusions

The prototype deployed for the desulfurization of biogas emitted from a closed landfill at the pilot scale demonstrated comparable desulfurization capacities with other biological desulfurization processes; with the added advantage of requiring a minimal energy input. A metastable operation zone between the 2FeOH^{2+} and Fe^{2+} was identified, considering the pH and ORP reached during the continuous desulfurization of sour biogas emitted from the closed landfill Prados de la Montaña in Mexico City. The capacity of treatment and then its energetic feasibility could be improved by finding the limits of treatment without increasing the operational energy consumption.

Author Contributions: Conceptualization, S.R., A.G.-S.; methodology, A.V., M.F.-M., L.A.A.-G., M.M.-Z., S.R., A.G.-S.; investigation, A.V., M.F.-M., L.A.A.-G., M.M.-Z.; resources, S.R., A.G.-S.; A.V., L.A.A.-G.; writing, A.V., L.A.A.-G., A.G.-S.; writing—review and editing, A.G.-S., S.R.; supervision, A.G.-S.; project administration, S.R.; funding acquisition, S.R., A.G.-S.

Conflicts of Interest: The authors declare no conflict of interest.

References

1.　Kigozi, R.; Muzenda, E.; Aboyade, A.O. Biogas technology: Current trends, opportunities and challanges. In Proceedings of the 6th International Conference GREEN Technology, Renewable Energy & Environmental Engineering, Cape Town, South Africa, 27–28 November 2014; pp. 311–317.

2.　Kuhn, J.N.; Elwell, A.C.; Elsayed, N.H.; Joseph, B. Requirements, techniques, and costs for contaminant removal from landfill gas. *Waste Manag.* **2017**, *63*, 246–256. [CrossRef] [PubMed]

3.　Awe, O.W.; Zhao, Y.; Nzihou, A.; Minh, D.P.; Lyczko, N. A Review of Biogas Utilisation, Purification and Upgrading Technologies. *Waste Biomass Valoriz.* **2017**, *8*, 267–283. [CrossRef]

4.　Bailon, A.L.; Hinge, J. *Biogas Upgrading Evaluation of Methods for H₂S Removal*; Danish Technological Institute: Taastrup, Denmark, 2014.

5.　Latosov, E.; Loorits, M.; Maaten, B.; Volkova, A.; Soosaar, S. Corrosive effects of H_2S and NH_3 on natural gas piping systems manufactured of carbon steel. *Energy Procedia* **2017**, *128*, 316–323. [CrossRef]

6.　González-Sánchez, A.; Revah, S.; Deshusses, M.A. Alkaline biofiltration of H_2S odors. *Sci. Technol.* **2008**, *42*, 7398–7404. [CrossRef] [PubMed]

7.   De Angelis, A.; Bellussi, G.; Pollesel, P.; Perego, C. New method for H$_2$S removal in acid solutions. *ChemSusChem* **2010**, *3*, 829–833. [CrossRef] [PubMed]

8.   Devinny, J.S.; Deshusses, M.A.; Webster, T.S. *Biofiltration for Air Pollution Control*, 1st ed.; Lewis Publishers: Boca Raton, FL, USA, 2017.

9.   Velasco, A.; Morgan-Sagastume, J.M.; González-Sánchez, A. Evaluation of a hybrid physicochemical/ biological technology to remove toxic H$_2$S from air with elemental sulfur recovery. *Chemosphere* **2019**, *222*, 732–741. [CrossRef] [PubMed]

10.   Meruane, G.; Vargas, T. Bacterial oxidation of ferrous iron by Acidithiobacillus. *Hydrometallurgy* **2003**, *71*, 149–158. [CrossRef]

11.   Alemzadeh, I.; Kahrizi, E.; Vossoughi, M. Bio-oxidation of ferrous ions by *Acidithiooobacillus ferrooxidans* in a monolithic bioreactor. *J. Chem. Technol. Biotechnol.* **2009**, *8*, 504–510. [CrossRef]

12.   Almenglo, F.; Ramírez, M.; Gómez, J.M.; Cantero, D.; Revah, S.; González-Sánchez, A. Effect of VOCs and methane in the biological oxidation of the ferrous ion by an acidophilic consortium. *Environ. Technol.* **2012**, *335*, 531–537. [CrossRef]

13.   Lin, W.-C.; Chen, Y.-P.; Tseng, C.-P. Pilot-scale chemical–biological system for efficient H$_2$S removal from biogas. *Bioresour. Technol.* **2013**, *135*, 283–291. [CrossRef]

14.   Abatzoglou, N.; Boivin, S. A review of biogas purification processes. *Biofuels Bioprod. Bioref.* **2009**, *3*, 42–71. [CrossRef]

15.   Silverman, M.P.; Lundgren, D.G. Studies on the chemoautotrophic iron bacterium Ferrobacillus ferrooxidans: I. An improved medium and a harvesting procedure for securing high cell yields. *J. Bacteriol.* **1959**, *77*, 642. [PubMed]

16.   Villanueva-Estrada, R.E.; Rocha-Miller, R.; Arvizu-Fernández, J.L.; Castro González, A. Energy production from biogas in a closed landfill: A case study of Prados de la Montaña, Mexico City. *Sustain. Energy Technol. Assess.* **2019**, *31*, 236–244. [CrossRef]

17.   Vogel, A.I. *A Text-Book of Quantitative Inorganic Analysis-Theory and Practice*; Longmans, Green and Co.: London, UK; New York, NY, USA; Toronto, ON, Canada, 2013.

18.   Daoud, J.; Karamanev, D. Formation of jarosite during Fe^{2+} oxidation by *Acidithiobacillus ferrooxidans*. *Miner. Eng.* **2006**, *19*, 960–967. [CrossRef]

19.   Ho, K.L.; Lin, W.C.; Chung, Y.C.; Chen, Y.P.; Tseng, C.P. Elimination of high concentration hydrogen sulfide and biogas purification by chemical-biological process. *Chemosphere* **2013**, *92*, 1396–1401. [CrossRef] [PubMed]

20.   Asai, S.; Yasuhiro, K.; Tadahiro, Y. Kinetics of absorption of hydrogen sulfide into aqueous Fe(III) solutions. *AIChE J.* **1990**, *36*, 1331–1338. [CrossRef]

21.   Demmink, J.F.; Beenackers, A.A.C.M. Gas desulfurization with ferric chelates of EDTA and HEDTA. *Ind. Eng. Chem. Res.* **1998**, *37*, 1444–1453. [CrossRef]

22.   Wubs, J.H.; Beenackers, A.A.C.M. Kinetics of the Oxidation of Ferrous Chelates of EDTA and HEDTA in Aqueous Solution. *Ind. Eng. Chem. Res.* **1993**, *11*, 2580–2594. [CrossRef]

23.   Asai, S.; Nakamura, H.; Aikawa, H. Absorption of hydrogen sulfide into aqueous ferric chloride solutions. *J. Chem. Eng. Jpn.* **1997**, *30*, 500–506. [CrossRef]

24.   De La Rosa, D.A.; Velasco, A.; Rosas, A.; Volke-Sepúlveda, T. Total gaseous mercury and volatile organic compounds measurements at five municipal solid waste disposal sites surrounding the Mexico City Metropolitan Area. *Atmos. Environ.* **2006**, *40*, 2079–2088. [CrossRef]

25.   Zhang, S.; Yan, L.; Xing, W.; Chen, P.; Zhang, Y.; Wang, W. *Acidithiobacillus ferrooxidans* and its potential application. *Extremophiles* **2018**, *22*, 563–579. [CrossRef]