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Editorial

Special Issue "Advances in Biogas Desulfurization"

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Abstract: This Special Issue contains three articles and two reviews. The biological reactors used in the studies were fed with real biogas from Landfill or STPs. One research article concerns the use of a pilot scale plant with a combined process with a chemical and biological system. The other two studies concern anoxic biotrickling filters, with one study focused on the study of variable operation and its optimization through the response surface methodology, and the other focused on the selection of packing material. The reviews concern the current state of biogas desulfurization technologies, including an economic analysis, and the microbial ecology in biofiltration units. This Issue highlights some of the most relevant aspects about biogas desulfurization.

Keywords: hydrogen sulfide; biogas; desulfurization; biotrickling filter; anoxic; response surface methodology; microbial ecology; sulfur-oxidizing bacteria; packing material; anaerobic digestion

1. Introduction

This Special Issue contains the invited submissions to a Special Issue of *ChemEngineering* on the topic "Advanced Biogas Desulfurization" [1–5]. Three research articles [1–3] and two reviews [4,5] have been published. Biogas is a renewable energy source produced by the biodegradation of organic matter under anaerobic conditions. The use of renewable energies is increasing due to global warming and the increasing price of fossil fuels. However, biogas needs to be desulfurized prior to use. The biogas composition mainly depends on the feedstock (sludge from sewage treatment plants (STPs), waste from the agri-food industry, the organic fraction of municipal solid waste, livestock manure, etc.), with the main components being methane (45–75%) and carbon dioxide (20–50%). However, hydrogen sulfide (H_2S) leads to corrosion and the combustion of non-desulfurized biogas produces the emission of SOx in flue gases. The H_2S concentration can range from a few ppm_V (0.5–700 ppm_V in landfill gas) up to more than 30,000 ppm_V in the plant's pulp-making process; and biogas flow rates can be in the range from several hundred cubic meters per hour (usually in STPs) to several thousand cubic meters per hour (usually in landfills). The applications of biogas are also wide-ranging, with the most common being burning in motors to produce electricity or electricity and heat. However, biogas can also be used as a fuel for solid oxide fuel cells or for hydrogen production by biogas reforming. Moreover, in the case of upgrading (CO_2 removal) biogas can be injected into the natural gas grid or used as fuel for vehicles. This wide range of biogas flow rates, H_2S concentrations, types of applications and purification requirements, as well as biogas sources, results in a wide variety of technologies, which can be subdivided into those that involve physicochemical phenomena and those that involve biological processes.

This Special Issue aims to bring together the scientific/technical advances on physicochemical and/or biological processes for biogas desulfurization. Biogas desulfurization is considered to be essential by many stakeholders (biogas producers, suppliers of biogas upgrading devices, gas traders, researchers, etc.) around the world, as the importance of biogas desulfurization to allow its valorization is well understood.

2. Brief Overview of the Contributions to This Special Issue

Velasco et al. [1] carried out the desulfurization of landfill biogas ('Prados de la Montaña', Mexico) at the pilot scale by a combined process involving chemical and biological treatments. In this study, an Absorption Bubble Column (ABC) was used in which H_2S was absorbed and oxidized to elemental sulfur by ferric sulfate. A biotrickling filter (BTF) was employed for ferric sulfate regeneration (oxidation of Fe^{2+} produced in the ABC to Fe^{3+}) by an enriched acidophilic mineral-oxidizing bacteria consortium (AMOB). The first reported application of an iron-based process and biological regeneration was reported in 1984 by Barium Chemical Ltd. and this approach is known as the Bio-SR process using *Acidithiobacillus ferrooxidans* and a jet-scrubber for H_2S oxidation. Since then, numerous configurations have been published, but the main drawbacks are related to the elemental sulfur separation and jarosite formation. Jarosite helps to develop the biofilm growth but it reduces the amount of Fe^{3+} and, therefore, its formation must be controlled, usually by controlling the pH. The effect of no pH control and no forced convection of air on the iron oxidation rates and H_2S removal were studied. In this study, removal efficiencies (REs) higher than 99.5% were achieved for H_2S concentrations in the range 120–250 ppm_V (Empty Bed Residence Time (EBRT) of 4.5 min in the ABC). The system was successfully operated for around seven months with minimal energy input and a metastable operation the zone between $2FeOH^{2+}$ and Fe^{2+}. However, elemental sulfur was accumulated on the packed bed of the BTF and this was not recovered in the settler due to its colloidal nature.

Almenglo et al. [2] studied the H_2S removal from biogas produced in an STP ('Bahía Gaditana', Cádiz, Spain) by an anoxic BTF at the pilot scale (packed bed volume of 0.167 m^3). The effect of the biogas flow rate, trickling liquid velocity (TLV) and nitrate concentration on the H_2S RE and elimination capacity (EC) were studied using a full factorial design (3^3). Anoxic biofiltration is a promising technology for biogas desulfurization because it avoids biogas dilution and reduces the risk of explosion when compared to aerobic BTFs. In fact, in the past seven years, there has been a significant increase in the number of published studies in this area. In this study, the highest H_2S RE values were obtained at a TLV of 15.27 m h^{-1}, with RE values of 99.53, 97.65 and 92.13% for EBRTs of 600, 200 and 120 s, respectively. Therefore, the maximum and critical ECs were 158.83 gS m^{-3} h^{-1} (RE 92.13%) and 34.93 gS m^{-3} h^{-1} (RE 99.53%), respectively. Higher values can be found in the literature for laboratory scale systems with a higher height:diameter ratio, but this pilot plant was one of the first anoxic BTFs to be installed in an STP, thus demonstrating the feasibility of this technology under real operating conditions (fluctuations in the biogas composition, weather, etc.). Moreover, experimental data were adjusted using Ottengraf's model, which allows the H_2S concentration along the bed to be predicted in a simple way. In contrast, dynamic models have been published previously by the same authors and this provided a better understanding of the process—although these models are more complex and are seldom used.

Tayar et al. [3] studied different packing materials for an anoxic BTF (packed bed volume of 3 L). One of the main drawbacks of BTFs, both aerobic and anoxic, is the clogging of the packed bed. Clogging can be caused by the accumulation of elemental sulfur and/or biomass growth. However, in most cases it is due to elemental sulfur accumulation, since the biofilm growth rate is low. It can be seen from the literature that elemental sulfur production can be controlled by increasing the electron acceptor feed (nitrate, nitrite or oxygen) but sulfur formation is unavoidable. In this respect, the selection of the packing material is critical as it will affect the amount of sulfur and biomass that can attach to the packing in the bed. In this study, four packing materials were tested: strips of polyvinyl chloride (PVC), polyethylene terephthalate (PET), polytetrafluoroethylene (Teflon®) and open-pore polyurethane foam (OPUF). PVC was chosen due to the high concentration of biomass, although it was lower than for OPUF, and its low cost. The BTF performance showed high H_2S removal (95.72%) and EC (98 gS m^{-3} h^{-1}), with values similar to those obtained in previous studies carried out with OPUF. Therefore, PVC could be a potential low-cost packing material for use in BTFs.

Okoro and Sun [4] submitted an interesting review about the current state of biogas desulfurization technologies: physicochemical, biological, in situ, and post-biogas desulfurization strategies. Moreover, a review of the annual operation and annualized capital cost per unit volume was carried out. To perform a cost analysis is a challenging undertaking and there are very few published studies. Biogas stakeholders could make decisions about the best technology based on these results. However, there are numerous factors that make the comparison complex: lack of data from companies, differences between studies (scale, source of biogas, etc.), location in different countries, supplies (prices of electricity, chemicals, etc.), etc. In this review, the authors carried out a thorough review; for instance, studies from member countries of the OECD and uncertainties about the 50–150% variation in the cost were considered. The study shows that in situ chemical dosing is the cheapest biogas desulfurization technique, although limitations were identified in terms of the system control costs and environmental impact due to the continuous chemical supply. Moreover, the integration of several technologies could be of interest to reduce the weaknesses of each desulfurization strategy.

Le Borgne and Baquerizo [5] present a review on the microbial ecology of biofiltration units for biogas desulfurization. Moreover, a review of the biofiltration technologies is included: conventional biofilter, BTF and bioscrubbers. Biological H_2S oxidation can be carried out under aerobic or anoxic conditions. Therefore, the main chemotrophic Sulfur Oxidizing Bacteria (SOB) will depend on the final electron acceptor. The review shows the microbial ecology in aerobic and anoxic BTFs through molecular techniques such as fingerprint methods (PCR-DGGE, T-RFLP), fluorescence in situ hybridization (FISH), or next generation sequencing technologies (450-pyrosequencing or Illumina platforms). As one would expect, the environmental conditions had a direct impact on the diversity of bacterial communities and their structure and dynamics. However, not enough is currently known about the role of the main populations in these bioreactors.

3. Gaps in Biogas Desulfurization

In the past 15 years, there have been significant advances in the development of biological desulfurization processes. However, there are still shortcomings that require further investigation. To my mind, one of the main issues is the formation of elemental sulfur in bioreactors with packing material, such as BTFs, although there has been a significant advance in the increase of the oxygen mass transfer in aerobic bioreactors, such as aerobic BTFs. In the case of anoxic bioreactors, it is possible to feed the system with high nitrate or nitrite concentrations, although this entails a significant cost (environmental and economic) in terms of the use of chemical compounds. However, the feasibility of feeding nitrified effluent from ammonium-rich wastewater has been demonstrated, thus avoiding the above impact. In any case, elemental sulfur formation is unavoidable and further research is needed to prevent its accumulation. A possible solution would be the use of suspended biomass bioreactors, in which clogging would be avoided. In these bioreactors, a new issue would be the separation of elemental sulfur in an economic way.

Another important gap is to determine the role of the key populations to avoid operational outages in the bioreactors. Likewise, progress can be made in the control systems by improving the mathematical model using the latest advances in microsensors. A microsensor has been developed to measure pH and O_2 profiles in the biofilm and, in this respect, it would be interesting to develop new microsensors to measure sulfide, nitrate and nitrite profiles.

A high priority area is the scaling-up of desulfurization technologies to the demonstration or industrial scales. Many of these systems have only reached the pilot scale, so it is necessary to develop larger plants in order to obtain long-term operational data, to determine the operational limits and to evaluate economic and environmental impacts. In this regard, some studies have already been carried out, but they are very scarce, and greater effort is needed in this direction. In other cases, such as aerobic BTFs, all of this information is available and a better dissemination in companies is necessary in order to increase the number of industrial plants. All of this information will allow the evaluation of these technologies and enable the installation of new plants. It is also necessary to reduce the gas residence time in order to design smaller equipment, minimize energy consumption and integrate desulfurization systems in plants to avoid the consumption of chemical reagents. Finally, it would be interesting to look for new biological processes for biogas revalorization. For instance, other value-added products could be obtained from the methane and carbon dioxide present in the biogas that can be integrated into the biological desulfurization processes.

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