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Biogas biological desulphurisation under extremely acidic conditions for energetic valorisation in Solid Oxide Fuel Cells

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HIGHLIGHTS

- A biotrickling filter was installed and operated at pilot-scale in a WWTP in Spain.
- Operating conditions for biogas desulphurisation at acidic environment were determined.
- An average elimination capacity of 169 $gH_2S\ m^{-3}\ h^{-1}$ was obtained on the long-term.
- Partial oxidation to elemental sulphur was envisaged to be the preferred mechanism.
- *Acidithiobacillus thiooxidans* was dominant on the microbial consortium.

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ABSTRACT

The most harmful biogas contaminant for energy conversion equipment such as fuel cells is hydrogen sulphide (H_2S); thus efficient and cost-effective treatment systems for this compound should be designed and developed. A pilot-scale biotrickling filter (BTF) working in acidic media (pH = 1.5–2) was operated for raw sewage biogas desulphurisation. Its operational performance as a function of two key important process parameters (temperature and retention time) was evaluated through short-term experimentation; showing that H_2S removal efficiencies greater than 90% can be obtained at temperatures of 30 °C, retention times of 80–85 s and H_2S Loading Rates of 210 $gH_2S/(m^3_{bed}\ h)$. The system was afterwards operated for 924 h and showed an average elimination capacity of 169 $gH_2S/(m^3_{bed}\ h)$ at an average removal efficiency of 84%. The unit proved to be reversible to the effect of operation disruptions (lack of temperature control, limitations on oxygen supply), which were introduced to simulate possible system miss functioning or operational failures. Nevertheless, partial oxidation to elemental sulphur ($S_{(s)}$) accounted for 70% of H_2S removal progressively increasing the pressure drop over the column; reducing the availability of the treatment line and eventually leading to fuel cell shutdowns. More efficient systems for oxygen supply and solids removal are the key factors to be addressed for a sustainable deployment of BTF technology in waste water treatment plants (WWTP).

1. Introduction

Within the framework of sustainable development, and ever-increasing energy costs, sewage biogas utilisation is one the main approaches today for wastewater treatment operators for on-site energy production [1,2]. Biogas contains a wide variety of contaminants like sulphur compounds, siloxanes, hydrocarbons and halogenated organic compounds. The most harmful for energy conversion equipment due to its presence up to 2000–5000 ppm_v is hydrogen sulphide (H_2S) [3], which can cause corrosion of metal parts, degrade engine's oil or fuel cell catalysts and form poisonous sulphur dioxide (SO_2) during combustion for electricity production [4]. Therefore, H_2S removal from biogas or other waste-derived fuels is required not only from health and safety reasons but for operational reasons. In this context, costly and energy consuming H_2S removal technologies must be installed upstream the energy conversion system in order to meet the respective inlet requirements (300–500 ppm_v for internal combustion engines; 1 ppm_v for fuel cells or grid injection) [5–7].

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There are numerous technologies currently available for biogas desulphurisation which can be classified as physical (absorption and adsorption using solid and liquid phases), chemical enhanced (chemical absorption using oxidising or alkaline solutions such as amines or soda), [8] and biological processes. Conventional chemical and physical H_2S removal technologies have large investment and operational costs; hence cost-effective biological treatments show very promising prospects [9] to increase the efficiency of biogas energy recovery.

Two main different biological technologies are available for biogas desulphurisation: bioscrubbers and biotrickling filters. On the one hand, bioscrubbers consist of a two-stage process: chemical H_2S absorption with an alkaline solution followed by a biological reactor for solution regeneration under aeration in a gas-lift type reactor [10]. These complex systems have high capital and operational costs; hence their application range is limited to large-scale biogas energy recovery plants [11]. On the other hand, in biotrickling filters (BTF), the overall process takes place in only one reactor; which reduces the investment cost of the unit. In these systems, pollutants are degraded by specific bacteria which grow onto a wet inorganic solid packing material. Although up to now biotrickling filters have been mostly applied to odour control [12,13], the growing interest on low cost biogas energy recovery on the recent years has led to the improvement of these systems to make them a suitable and reliable technology for the desulphurisation of highly contaminated biogas [14].

H_2S and other sulphur species are first transferred from the biogas matrix to the interface between a water layer and the biofilm and later absorb and diffuse into the biofilm where are metabolised into elemental sulphur and sulphuric acid by sulphur oxidising bacteria (SOB) namely *Thiobacillus* sp. The moving layer of water in BTF, which is generally circulated from a storage tank, ensures high water content in the biofilm, while providing some degree of control of the biofilm's growing rate, encouraging sloughing and reducing clogging. Water (which may be co-current or counter-current to the biogas flow) carries the pollutant downward and can be recirculated, causing some reduction on the removal efficiency. Treated water from the wastewater treatment plant (WWTP) can be used as a source of water and nutrients for the biological activity.

Kuenen [15] proposed the H_2S removal mechanism to occur through a series of physico-chemical processes and biological reactions, which are summarised by Eqs. (1)–(4).

(a) $H_2S_{(g)}$ dissolution in water

$$H_2S_{(g)} \rightarrow H_2S_{aq} \tag{1}$$

(b) H_2S biological oxidation to SO_4^{-2}

$$H_2S_{(aq)} + 2O_{2(g)} \rightarrow 2H^+ + SO_4^{2-} \tag{2}$$

(c) H_2S biological oxidation to $S_{(s)}$

$$2H_2S_{aq} + O_{2(g)} \rightarrow 2S^0_{(s)} + 2H_2O \tag{3}$$

(d) $S_{(s)}$ biological oxidation to SO_4^{-2}

$$2S^0_{(s)} + 3O_{2(g)} + 2H_2O \rightarrow 2H^+ + SO_4^{2-} \tag{4}$$

All four processes result in pH, dissolved oxygen and oxidation–reduction potential (ORP) modifications, which can be used for monitoring and control of process performance [16,17]. Other reactions, such as the non-biological oxidation of H_2S to thio-sulphate and the further biological oxidation of thio-sulphate to sulphuric acid, have also been reported, but they are of less relevance [17,18]. Gabriel et al. [10] depicted the stoichiometry of the combined reaction of H_2S oxidation (both partial and full) with autotrophic biomass synthesis; assigning a fraction of 80–20% of the electrons transferred to the two processes.

Progressive filter clogging over the long term has often been described as the most important operational limitation for the industrial application of BTF [13,19,20]. Clogging can be the result of accumulation of elemental sulphur (due to partial H_2S oxidation described by Eq. (3)), inert and active biomass and gypsum (by combination of calcium cations from make-up water and sulphate anions from H_2S full oxidation, [20]) in the contact surface where the biological degradation takes place. This accumulation strongly affects system's operation and performance, since the available cross section area of packing material is dramatically decreased, thus reducing the contact time between biogas and SOB and affecting then H_2S removal efficiency. Under highly loaded BTF, elemental sulphur formation is regarded as the most significant factor affecting filter clogging.

In this context, full oxidation of hydrogen sulphide into sulphuric acid (as described by Eqs. (2) and (4)) reduces filter clogging and in turn leads to a dramatic reduction on the pH. According to the acid–base equilibrium (pK_{a1} (H_2S/HS^-) = 6.9 at 25 °C), neutral to basic pH values favour the gas–liquid partitioning of H_2S (Henry constant = H = 10 (l·atm)/mol at 25 °C) [21], from the gas to the aqueous phases by formation of HS^- ions; hence these conditions have been mainly used by other authors for biogas biological desulphurisation [19,22–24]. However, pH control is expensive and difficult to maintain; with the requirement of constant addition of alkalis (p.e.: NaOH) or other buffer solutions. Furthermore, when wastewater effluent is used as liquid phase and the BTF is operated at neutral/basic pH conditions, other bacterial cultures (e.g. nitrification, organic matter oxidation, methane oxidation, etc.) can also grow on the biofilm because of the residual organic matter and nutrient contents; competing in this way with SOB for p.e.: oxygen. Moreover, as heterotrophic biomass growth yield is greater than autotrophic biomass, biofilm growth on these conditions would also contribute to filter clogging; resulting in more frequent cleaning operations and consequently reducing the availability (running hours/total hours) of the BTF.

The aim of this paper is to validate and assess at pilot scale extremely acidic biotrickling filters for biogas desulphurisation and to describe its performance by a simplified mathematical model. This work describes the experimental pilot plant results, evaluating the effect of temperature and retention time on the short-term performance and assessing the suitability of biotrickling filters for biogas desulphurisation at the long-term operation.

2. Methodology

2.1. Biogas powered Solid Oxide Fuel Cell pilot plant site description

The biogas-powered Solid Oxide Fuel Cell (SOFC) pilot plant was installed at Mataró WWTP. This WWTP collects wastewater from different towns and villages in the Maresme region (North-East of Barcelona, Spain). The sewage treatment capacity is 30,000 m^3/day and biogas production accounts for 190 Nm^3/h; the vast majority of which is used for district heating and cooling in public buildings (hospitals, schools, public buildings, etc.). The pilot plant treated 10 Nm^3/h, representing around 5% footprint of the full-scale.

2.2. Description of the SOFC pilot experimental setup

The pilot-scale biotrickling filter used in this study (Fig. 1) was part of a bigger biogas valorisation plant, which consisted of, apart from the BTF, a polishing stage (adsorption on iron containing adsorbent, drying and activated carbon) and a SOFC for on-site electricity and thermal energy production. The BTF unit was made with a column black polypropylene (PP); square-section of