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Effect of gas-liquid flow pattern and microbial diversity analysis of a pilot-scale biotrickling filter for anoxic biogas desulfurization

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HIGHLIGHTS

- Alternative operation between co- and counter-current enhance the carrier lifetime.
- Elemental Sulfur cleaning can be carried out stopping the biogas feeding.
- *Sedimenticola* was consider the main desulfurizing bacteria.
- Single-pass reduce the H_2S elimination capacity.

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ABSTRACT

Hydrogen sulfide removal from biogas was studied under anoxic conditions in a pilot-scale biotrickling filter operated under counter- and co-current gas-liquid flow patterns. The best performance was found under counter-current conditions (maximum elimination capacity of 140 gS m^{-3} h^{-1}). Nevertheless, switching conditions between co- and counter-current flow lead to a favorable redistribution of biomass and elemental sulfur along the bed height. Moreover, elemental sulfur was oxidized to sulfate when the feeding biogas was disconnected and the supply of nitrate (electron acceptor) was maintained. Removal of elemental sulfur was important to prevent clogging in the packed bed and, thereby, to increase the lifespan of the packed bed between maintenance episodes. The larger elemental sulfur removal rate during shutdowns was 59.1 gS m^{-3} h^{-1}. Tag-encoded FLX amplicon pyrosequencing was used to study the diversity of bacteria under co-current flow pattern with liquid recirculation and counter-current mode with a single-pass flow of the liquid phase. The main desulfurizing bacteria were *Sedimenticola* while significant role of heterotrophic, opportunistic species was envisaged. Remarkable differences between communities were found when a single-pass flow of industrial water was fed to the biotrickling filter.

1. Introduction

Sulfide oxidation coupled to denitrification by sulfide-oxidizing nitrate-reducing bacteria (SO-NR) in anoxic biotrickling filters (BTFs) has been shown as an alternative for biogas desulfurization. Overall, the process is similar to the aerobic process in terms of reactor design, packing material and operating conditions (Almenglo et al., 2016; Montebello et al., 2014; Soreanu et al., 2008). The main difference lays in the use of nitrate as electron acceptor instead of oxygen. Nitrate use leads to no biogas dilution, thus no energy potential of biogas is lost, coupled to a reduced risk of explosion compared to that of oxygen.

Most BTFs for biogas desulfurization operate under a counter-current configuration (Muñoz et al., 2015). However, recently was found that oxygen mass transfer efficiency in the packed bed of an aerobic BTF filled with plastic Pall rings was more favorable in the case of a co-current configuration (López et al., 2016). The sulfate production capacity was 102.8 gS-H_2S m^{-3} h^{-1} and 78.8 gS-H_2S

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m^{-3} h^{-1} for co-current and counter-current flow modes, respectively.

Despite the recent advances in the analysis of the impact of process variables on system performance both at laboratory and at pilot-scale, dynamics of microbial communities in anoxic biotrickling filters has been poorly referenced. There are many biological techniques to assess the microbial diversity as well as its evolution along time such as banding patterns from denaturing gradient gel electrophoresis (DGGE), fluorescence in-situ hybridization (FISH), terminal restriction fragment length polymorphism (T-RFLP) and pyrosequencing. However, pyrosequencing has been shown as one of the most powerful tools to analyze and quantify the microbial composition and abundance of biomass in bioreactors under different operating conditions (Cheng et al., 2016; Portune et al., 2014; Montebello et al., 2013). To the authors' knowledge, no microbial analysis base on pyrosequencing has been performed in anoxic BTFs.

In the present work, the effect of the co- and counter-current G-L flows and the effect of a single-pass of supplied industrial water were assessed on bioreactor performance as well as on the microbial diversity and its dynamics based on Tag-encoded FLX amplicon pyrosequencing (bTEFAP).

2. Materials and methods

2.1. Experimental equipment and analytical methods

An anoxic BTF at pilot-scale was used, which characteristics can be found elsewhere (Almenglo et al., 2016). The column diameter and packing bed height were 0.5 and 0.85 m, respectively. Randomly filled, open-pore polyurethane foam (PUF) cubes of 125 cm^3 each were used as packing material. The BTF was installed at the 'Bahía Gaditana' (San Fernando, Spain) wastewater treatment plant (WWTP) and fed with a biogas split from one of their full-scale anaerobic digesters. Thus, temperature and pH were not controlled. Industrial water (IW) from the WWTP was used to feed the BTF. The IW was supplemented with a nitrate concentrate solution as described by Almenglo et al. (2016).

The biotrickling was operated for a period of 415 days in five well-differenced operational periods. The first 297 days the BTF was operated in counter-current mode, then the biogas was fed in co-current for 63 days (days 298–360). After that, the biogas supply was disconnected to allow the removal of elemental sulfur for 7 days (days 361–367) and returned to counter-current for 34 days (days 368–401) to reach steady-state conditions before the single-pass flow study for 14 days (days 402–415).

The CH_4, CO_2 and H_2S concentrations in the biogas stream were measured using a gas chromatograph (GC–450, BRUKER, Germany). A specific gas sensor (GA2000Plus, Fonotest Instruments S.L., Spain) was used for field measurements. Sulfate, nitrite and nitrate were measured by colorimetric methods (Almenglo et al., 2016; Clesceri et al., 1999). Sulfide was measured using an ion-selective electrode (ISE) for sulfide combined with an Ag/AgCl electrode as reference (sympHony™ Meter, VWR International Inc., USA). Dissolved oxygen (DO) was measured using a polarographic sensor (YSI MODEL 95, YSI incorporated, USA).

2.2. Mass transfer coefficient determination

The gas-liquid mass transfer coefficient was determined using pristine PUF and IW. Initially, a biogas stream was passed through the column to desorb DO. Then, an air stream was fed to the BTF while DO was recorded at the inlet and outlet of the packed bed (T = 22.6 ± 0.8 °C). The water phase was continuously recirculated from bottom to top of the BTF. Same considerations as these applied by Dorado et al. (2009) were assumed in order to obtain equations (1)–(3).

$$Q_L\left(C_{L,out}-C_{L,in}\right)=K_L a V_C \frac{\left(\frac{C_{G,in}}{H}-C_{L,out}\right)-\left(\frac{C_{G,out}}{H}-C_{L,in}\right)}{\ln\left(\frac{\left(\frac{C_{G,in}}{H}-C_{L,out}\right)}{\left(\frac{C_{G,out}}{H}-C_{L,in}\right)}\right)} \tag{1}$$

$$f_1(C)=V_C \frac{\left(\frac{C_{G,in}}{H}-C_{L,out}\right)-\left(\frac{C_{G,out}}{H}-C_{L,in}\right)}{\ln\left(\frac{\left(\frac{C_{G,in}}{H}-C_{L,out}\right)}{\left(\frac{C_{G,out}}{H}-C_{L,in}\right)}\right)} \tag{2}$$

$$Q_L\left(C_{L,out}-C_{L,in}\right)=K_L a f_1(C) \tag{3}$$

Where Q_L is the liquid flow rate (m^3 h^{-1}); $C_{L,out}$ and $C_{L,in}$ are the outlet and inlet DO concentration (g O_2 m^{-3}) of the packed bed, respectively; $C_{G,out}$ and $C_{g,in}$ are the outlet and inlet O_2 concentrations (g O_2 m^{-3}) of the packed bed, respectively; K_L is the global liquid mass transfer coefficient (m h^{-1}); a is the interfacial area (m^2 m^{-3}); V_C is the packing volume (m^3) and H is the dimensionless gas-liquid Henry coefficient.

A full factorial design (3^2) was performed for Q (1, 3 and 5.2 m^3 h^{-1}) and Q_L (1, 2 and 3 m^3 h^{-1}). The global mass transfer coefficient was determined in both flow modes (co- and counter-current), thus, notice that $C_{L,out}$, $C_{L,in}$, $C_{G,out}$ and $C_{g,in}$ corresponded either to the top or bottom concentrations of the packed bed depending on the flow mode under analysis.

2.3. Co-current and counter-current flow operation mode

The operating conditions of the BTF are summarized in Table 1. The effect of increasing H_2S inlet loads (IL) was assessed under counter-current flow mode (Fig. 1a) and co-current flow mode (Fig. 1b) during 297 and 63 days, respectively. The operating conditions were maintained constant for at least for 24 h and 0.75 h in the long- and short-duration experiments, respectively. Under co-current flow the effect of increasing IL was carried out through short-time experiments.

In both operation flow modes, the nitrate concentrate solution was added automatically using a feeding control strategy based on the oxidation-reduction potential (ORP) measurement (Almenglo et al., 2016). In short, a fixed volume of the liquid sump was purged when an ORP set-point of −365 mV was reached and automatically replaced with IW. Such volume was defined as ten times the volume of the nitrate concentrate solution added.

2.4. Elemental sulfur de-accumulation experiments

Sulfur mass balances were carried out under counter-current operation to assess the mass of elemental sulfur removed in the BTF. Q and Q_L were kept constant at 3 m^3 h^{-1}. Four experiments of 18 h each were carried out at different maximum nitrate concentrations of 299.8, 149.2, 69.3 and 9.1 mg N-NO_3^- L^{-1}. First, an average inlet H_2S concentration of 5.29 ± 0.68 gS m^{-3} was fed, which corresponded to N:S ratios consumed ranging from 0.96 to 1.25 mol-N mol-S^{-1}. Later, a period of 136 h without biogas supply was decided in order to reduce the elemental sulfur accumulation in the packed bed.