Simultaneous removal of ammonium from landfill leachate and hydrogen sulphide from biogas using a two-stage oxic-anoxic system

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Biogas is a renewable energy source whose exploitation helps to reduce the use of fossil fuels and greenhouse gases (GHG) emissions. Biogas is primarily composed of methane (CH_4) (40-75%), carbon dioxide (CO_2) (25-55%) and other compounds in minor quantities. Although some of these trace compounds are innocuous, the mere presence of others, like H_2S, preclude biogas revalorization. H_2S removal becomes necessary because of its toxicity to human health and other serious problems like corrosion or SOx emissions (Ramírez et al., 2015). Anoxic biodesulfurization processes have numerous advantages over aerobic biodesulfurization like the existence of a simultaneous process of denitrification, reduction of explosion risks, null biogas dilution and lower transfer limitations (Fernández et al., 2014). Anoxic desulfurization of biogas has been traditionally carried out in biotrickling filters (BTFs), showing robustness and high removal efficiencies. However, problems caused by elemental sulphur accumulation or excessive biomass growth on the packing bed force to do periodical maintenance, stopping the biogas feeding. Moreover, BTFs are not able to work at low nitrogen/sulphur (N/S) ratios to produce elemental sulphur, which could be a marketable product. In the present work, the use of an airlift bioreactor for anoxic desulfurization is proposed. By this way, lacking a support in which become adhered to, the elemental sulphur would be easily recovered for different purposes like sulphuric acid production, fertilizer industry, etc. The elemental sulphur selectivity depends on the nitrogen/sulphur (N/S) ratio (Cano et al., 2019). Therefore, the optimal dosage of nitrate/nitrite should be supplied to the bioreactor in order to avoid extra operation costs, obtain a high elemental sulphur selectivity and maintain and outlet H_2S concentration below the target limit. Bearing that in mind, some feedback control strategies have been already implemented in anoxic biodesulfurization processes (Brito et al., 2017). In the present work, a proportional-integral (PI) feedback control strategy was implemented. Despite all advantages, anoxic desulfurization is associated with higher operational costs due to the large requirements of the electron acceptor (nitrate/nitrite) if their came from a chemical supplier (Cano et al., 2018). A feasible solution could be the use of the outflow of a nitrification reactor. By this way, two pollutants (NH_4^+ and H_2S) could be removed in a same process, obtaining desulfurized biogas and an ammonium and nitrate free effluent rich in recoverable elemental sulphur. It is possible to find a large variety of ammonium-rich effluents from industries. Among these effluents, landfill leachates (LL), originated from the rain water percolation through the landfilled solid waste and the moisture within itself, stand as one of most concentrated in ammonia effluents (Show et al., 2019).

Therefore, the main objective of the present work was to study the feasibility of a two-stage process, which consist on a nitrification bioreactor follow by a suspended biomass bioreactor (air-lift) under anoxic conditions. At a first stage, the integration was carried out by feeding synthetic wastewater (SW) with added ammonia as chemical reactant (NH_4Cl) to the nitrification bioreactor while at a second stage, SW was replaced by LL.

The integrated system was operated for 149 days. Nitrification of the ammonia-rich effluents was carried out in a 3L continuous stirred tank reactor (CSTR) (*Applikon Biotechnology BV, The Netherlands*) with biomass recirculation using a settler, at temperature of 30 ± 0.5ºC, pH of 8 and a DO < 1.5 mg O_2 L^{-1}. pH was controlled by the addition of $NaHCO_3$ (50 g L^{-1}) and H_3PO_4 (2N). SW was composed by NH_4Cl to a concentration of 1.1 g $N\text{-}NH_4^+$ L^{-1} supplemented with nutrients coming from a commercial NPK fertilizer 6-4-6 (*Infertosa, Spain*). In order to compare the performance of the system in the same conditions, LL was diluted with tap water to a concentration of 1.1 g $N\text{-}NH_4^+$ L^{-1}. Anoxic desulfurization was performed in an inner loop jacketed airlift bioreactor 3L fed with biogas mimic (mixture of H_2S and N_2) and controlled by two mass-flow controllers (*Bronkhorst High-Tech B.V., The Netherlands*).

Aiming to compare the integrated system performance, 3 experiments were accomplished. All these experiments were carried out under a PI control in which the outlet H_2S concentration (H_2S_{out}) was used as controlled variable, while nitrite/nitrate and ammonia feeding was used as manipulated variable. Experiment 1 consisted of decreasing the gas residence time (GRT) from 104 to 41 s maintaining constant the inlet H_2S concentration (H_2S_{in}) at 900 ppm_v, corresponding to an H_2S inlet load (IL) increase from 41 to 104 g $S\text{-}H_2S$ m^{-3} h^{-1}. This IL raise led to a decrease on the hydraulic residence time (HRT) of both bioreactors so these experiments

allowed to investigate the effect of GRT, HRT and IL increase on the integrated process. The experiments concluded when steady state was reached. Then, in order to test its robustness, the integrated system was tested under variable H_2S IL (56-104 gS-H_2S h^{-1} m^{-3}) according to staircase steps simulating disturbances in the inlet H_2S concentration (Experiment 2). Finally, in order to study the system limits, experiment 3 was carried out in which an IL increase (100-150 gS-H_2S m^{-3} h^{-1}) was applied to the bioreactor when LL was used as ammonium source.

During experiment 1, the H_2S removal efficiency (RE) was successfully maintained at 95%. Fig.1(a) shows the biomass concentrations during experiment ,1 when SW and LL were fed to the system. It can be seen that at same ILs, LL affects to desulfurization biomass growth leading to a lower concentration of biomass. Despite, this fact did not affect RE, elemental sulphur production was slightly affected, being 91 ± 2% and 83 ± 8% when SW and LL were fed, respectively. Generally, the HRTs obtained during experiment 1 were lower (47 to 19h) when LL was fed in comparison to SW (53 to 34h). Average ammonium removal efficiencies were similar when SW and LL were fed to the bioreactor being 86.5 ± 9.4% and 86.7 ± 9.9%, respectively.

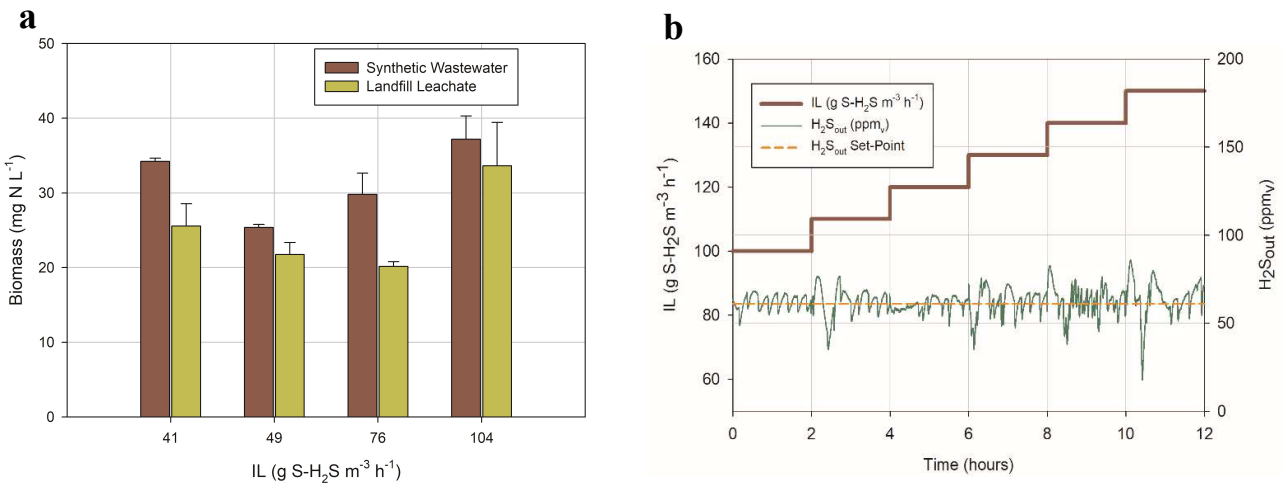

Figure 1. (a) Sulphide oxidizing biomass concentration at different ILs. (b) H_2S concentration present in the outlet under increasing ILs.

Experiment 2 demonstrated the system strength to maintain the RE under variable IL staircase steps. While small differences were found in RE using SW (94.6 ± 2.3%) and LL (93.7 ± 0.7%), HRT values were fairly lower when LL was fed (16.7 ± 4.4 h) versus SW (47.4 ± 22.9 h). Experiment 3 data is displayed in Fig 1(b). The system was able to kept the H_2S_{out} concentration stable under a set-point of 61 ppm_v with an average offset of 5.74 ± 5.21 ppm_v reaching a maximum elimination capacity of 144.6 g S-H_2S m^{-3} h^{-1} (RE = 96.4%).

In conclusion, in the present work a novel integrated system to biologically remove NH_4 and H_2S was successfully operated. Vague differences were found using SW and LL, demonstrating the real application feasibility of this technology.

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