# Bioprocess for simultaneous biogas landfill desulfurization and nitrogen removal from leachate in a pilot plant.

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Biogas is produced by the biodegradation of organic matter under anaerobic conditions. The main substrates used for biogas production are the organic fraction from municipal solid wastes (e.g. landfilling) and sewage sludge from wastewater treatment plants. Therefore, biogas is a renewable energy source, which is rich in methane (45-80%) and carbon dioxide (20-50%) but also contains hydrogen sulfide ($H_2S$) as the main pollutant. The $H_2S$ concentrations are in the range from 0.1% to 2% v/v (1,000-20,000 ppmv) (Arellano et al. 2017). Moreover, an additional issue in landfill is the leachate production. Ammonium removal from leachates are generally treated by physical-chemical technologies, such as coagulation-flocculation and vacuum evaporation. However, leachates can also be treated in biological reactors in a nitrification-denitrification process (Berge et al., 2005). Nitrification is two-step aerobic process, first ammonia is oxidized to nitrite (equation 1) and then to nitrate (equation 2), according the following equations:

$$NH_4^+ + 3/2\ O_2 \rightarrow NO_2^- + 2\ H^+ + 2\ H_2O \quad \text{(biological)} \quad (1)$$
$$NO_2^- + ½\ O_2 \rightarrow NO_3^- \quad \text{(biological)} \quad (2)$$

Biogas utilization as a typical energy-rich gas requires the removal of sulfur compounds before energy recovery processes to avoid problems of corrosion in internal combustion engines as well as for human health and environmental protection. Biological desulfurization in biotrickling filters (BTFs) and/or bioscrubbers have proven to be technically and economically effective alternatives to traditional physicochemical processes, especially for low $H_2S$ concentrations (Devinny et al, 1999), but also for high $H_2S$ concentrations, with elimination capacities (EC) as high as 280 g $H_2S$ $m^{-3}$ $h^{-1}$ under neutrophilic conditions (Fortuny et al. 2008) and 305 g $H_2S$ $m^{-3}$ $h^{-1}$ under anoxic conditions (Cano et al., 2019). Anoxic biogas desulfurization has several advantages, e.g., the high solubility of nitrate avoids mass transfer limitations. Besides, biogas dilution is avoided and the risk of explosion due to oxygen (air) injection is avoided. Despite these advantages, anoxic desulfurization is associated with higher operational costs due to the (usually) commercial source of the final electron acceptor. However, the operational cost of anoxic desulfurization can be reduced if nitrate or nitrate are produced in a nitrification bioreactor from ammonia-rich water effluents (Cano et al., 2018; Zeng et al., 2019). In anoxic conditions, the final electron acceptor for the hydrogen sulfide oxidation is nitrate or nitrite, according the following equations (Brito et al., 2018):

$$5\ H_2S + 2\ NO_3^- \rightarrow 5\ S^0 + N_2 + 4\ H_2O + 2\ OH^- \quad \text{(biological)} \quad (3)$$
$$5\ H_2S + 8\ NO_3^- \rightarrow 5\ SO_4^{2-} + 4\ N_2 + 4\ H_2O + 2\ H^+ \quad \text{(biological)} \quad (4)$$
$$3\ HS^- + 2\ NO_2^- + 5\ H^+ \rightarrow 3\ S^0 + N_2 + 4\ H_2O \quad \text{(biological)} \quad (5)$$
$$3\ HS^- + 8\ NO_2^- + 5\ H^+ \rightarrow 3\ SO_4^{2-} + 4\ N_2 + 4\ H_2O \quad \text{(biological)} \quad (6)$$

As shown, nitrate or nitrite denitrification can be done by autotrophic microorganism using water with high sulfide concentration. In anoxic bioreactors, the main desulfurizing bacteria identified have been *Sedimenticola* (Almenglo et al., 2016) and *Sulfurimonas* (Zeng et al., 2019).

In this study, the design and construction of a pilot-scale plant to treat a minimum biogas flow rate of 50 $Nm^3$ $h^{-1}$ will be carried out. The designed prototype will couple two biotechnologies for biogas desulfurization using ammonia-rich leachate. The two-steps process will be catalyzed by specialized microorganisms. Ammonia-oxidizing bacteria (AOB) will be used in a nitrifying bioreactor in order to obtain the nitrate solution to be used in the desulfurizing process. And, nitrate-reducing, sulfide-oxidizing bacteria (NR-SOB) will be used in the anoxic bioreactor for sulfide oxidation to elemental sulfur (equation 3).

Figure 1 shows the process diagram of the proposed technology. The bioprocess, called BIOGASNET, has four main steps. Firstly, the oxidation of the ammonium present in the leachate to nitrate in a sequential batch bioreactor (Figure 1, number 1). Secondly, the sulfide absorption from the biogas to the liquid in a scrubber (Figure 1, number 3). Thirdly, the sulfide oxidation to elemental sulfur in anoxic conditions (Figure 1, number 4). And finally, the elemental sulfur separation by sedimentation (Figure 1, number 5). This new process has been designed to overcome the main limitation of anoxic desulfurization (high operational cost for nitrate addition) and to obtain a value-added product (elemental sulfur). Related to this, the LIFE BIOGASNET project will demonstrate cost-efficient, low-carbon footprint technologies for biogas upgrading in order to boost the use of biogas as sustainable energy source, to reduce the carbon footprint of the energy cycle and to promote the circular economy.

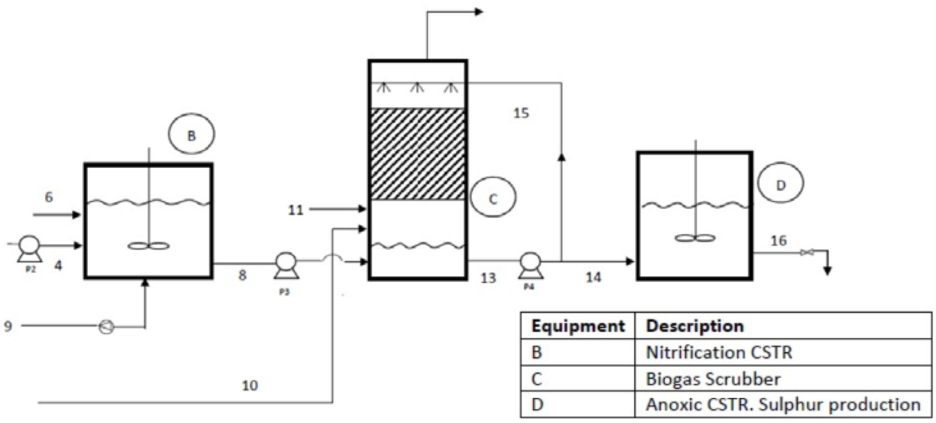


**Figure 1.** Process flow diagram. 4. Leachate. 6. Make-up water and nutrients. 8. Nitrate rich solution. 9. Air. 5. Settler. 10. Biogas. 11. Nutrients. 12. Clean Biogas. 13-15. Recirculation. 16. Elemental sulfur.

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