Moving Bed BioTrickling Filter for hydrogen sulphide removal from gas streams

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Abstract
A full scale prototype of an innovative MBBTF (Moving Bed BioTrickling Filter) for gaseous effluents treatment was designed and installed in a tannery wastewater treatment plant (Cuoiodepur, Pisa - Italy). The prototype treats 8000 m$^3$h$^{-1}$ of gaseous effluent in average with an hydrogen sulphide concentration of up to 300 mg m$^3$. The reactor was operated for 6 months in varying conditions (with an average removal in the range 10 to 18 Kg S-H$_2$S d$^{-1}$) and the rotation of the bed was demonstrated to be a suitable solution to promote the detachment of biomass and, as a result, for the control of pressure head loss caused by biofilm growth. This work report on the start-up phase and on the preliminary evaluation of the process conditions including pH, recirculated water flow rate and rotation frequency.

Keywords
Biological reactor, gas treatment, hydrogen sulfide removal, Moving Bed BioTrickling Filter.

INTRODUCTION
Hydrogen sulfide (H$_2$S) and organo sulfur compounds can be found in wastewater and biogas, causing corrosion, toxicity and odours problems. These compounds represent a major problem associated with anaerobic treatment of sulfate and sulfite containing wastewater (Syed et al., 2006). Chemical scrubbers are the most common technology applied for H$_2$S removal from gaseous effluents (Charron et al., 2004); however, this technology presents high costs, from both environmental and economic point of views due to the consumption of reagents and energy. Biological systems represent a possible alternative (Omri et al., 2011), however, conventional (static bed) biotrickling filter, are prone to clogging due to biofilm growth with the consequence of increasing energy consumption for gas pumping (Mannucci et al., 2012).

Biotrickling filter was used also for biological sweetening of energy gases (Fortuny et al., 2008) and biogas (Rodriguez, 2014). In both cases long-term performance struggles with reactor clogging with sulfur. In energy gases treatment they tested a washing phase. In biogas treatment the oxygen supply system, based on direct injection of air to the liquid phase, has demonstrated to be inefficient for a long-term operation leading to elemental sulfur accumulation in the packing material (i.e. promoting clogging episodes). The authors try the following unblocking strategy: oxidation of biologically produced elemental sulfur under neutrophilic conditions. The wash out strategy is based on the principle that the same microorganisms that degrade H$_2$S are capable of degrading the elemental sulfur into sulfate.

The clogging is particularly problematic when the load, in terms of Kg of H$_2$S per day is high, since the proneness to clogging is accelerated and can be compensated only by increasing the volume of the reactor. this is the case of tannery wastewater where sulphide concentration is in the range of 100 to 300 mg S L$^{-1}$ and sulphate concentration can reach up to 2 g L$^{-1}$; given the fact that and sulphate reduction may easily occur in equalisation and thickening tanks, the potential H$_2$S desorption may significantly increase the cost of gaseous effluents treatment.
The possibility of removing the biofilm and, consequently to optimize the solids retention time (SRT) in the trickling filter, would allow to limit clogging and maintain a high volumetric removal capacity, however, in order to develop the knowledge needed to optimise the SRT and other key process parameters, several aspects of the biological process need to be investigated, regarding the kinetics and the stoichiometry of sulphide oxidizing bacteria. In the literature, there are very few works on the main parameters related to biomass production by SOB, among which, the decay coefficient and the yield coefficient play a key role.

In literature there are few estimations of the endogenous decay coefficient for SOB and kinetic and stoichiometric characterization. Munz et al. (2009) use combined respirometric and titrimetric techniques in order to estimate \( \beta_{\text{SOB}} \) (0.13 \( \text{d}^{-1} \)). Mora et al used titrimetric and respirometric to study the sulfide-oxidizing nitrate-reducing consortia. A growth yield of 0.328±0.045 g VSS/g S was calculated after 350 h of operation when steady-state conditions were reached (Mora et al. 2014). However, these estimates were made at pH close to neutrality and using thiosulfate (as reduced form of sulfur) instead sulfide.

In the context of the UE LIFE+ Project BIOSUR (Rotating Bioreactors for sustainable hydrogen sulphide Removal), a full scale prototype of a moving bed biological reactor (MBBTF-Mobile Bed BioTrickling Filter) was designed and constructed with the aim of using the biodiscs rotation as innovative strategy for excess biomass removal, thanks to the shear stress between biodiscs and water in the bottom part of the MBBTF. We tested the prototype with aerobic condition but it is possible to treat the biogas stream with nitrite and nitrate.

**MATERIALS AND METHODS**

**Prototype**
The MBBTF has a cylindrical shape and is divided into four sectors. Each sector contains a biodisc (diameter 2.38 meter). Within each sector there is 40 cm of water depth and each of them is hydraulically separated up to an height of 50 cm. The water from each sector is pumped to an external tank and recirculated over the biodiscs to keep them wet and to mix the substrates in the water phase. Nutrients (nitrogen and phosphorus) are dosed in the recirculation flow, the concentration of nutrients is controlled in order to avoid limitation of biomass growth. Since biological oxidation of \( \text{H}_2\text{S} \) produces acidity (Chaiprapat et al., 2011), make up water is added for the maintenance of the pH setpoint; the water level in the MBBTF is kept constant and the excess water discharged. The biomass is immobilized on rotating discs (with horizontal axis) filled with polyurethane foam partially submerged in water, the total volume of the bed is 8 m\(^3\). The rotation of the discs (and eventually the use of washing solution), allows to apply shear stress on the biofilm in order to remove the excess biomass with the goal of controlling pressure head loss. The MBBTF has been implemented in the treatment train of the existing tannery wastewater treatment plant operated by Cuoiodepur (Pisa, Italy). The prototype is designed to treat up to 12000 m\(^3\)h\(^{-1}\) and inlet concentrations of \( \text{H}_2\text{S} \) variables within a range of 50 to 400 mg m\(^{-3}\). The MBBTF is connected to the piping network that carry contaminated air from the wastewater treatment tanks of Cuoiodepur to the chemical scrubbers. The flow of contaminated air crosses horizontally the MBBTF. The prototype is located close to the chemical scrubbers. The chemical scrubber are six vertical tower and two horizontal for the finishing. The towers remove \( \text{H}_2\text{S} \) by washing in countercurrent with strongly basic solution. The prototype intercepts the gas stream from the thickener because is very rich of \( \text{H}_2\text{S} \).

**Reactor start up**
A completely mixed reactor of one cubic meter was used for *inoculum* preparation by dosing 300 L of water, 15 L of primary sludge and 15 L of biological sludge from Cuoiodepur and a solution of sodium sulfide (NaS) with S concentration of 1 g L\(^{-1}\). The pH setpoint was 3 and oxygen was
supplied through a diffuser membrane on the bottom of the reactor. Once ready the inoculum was poured inside the liquid recirculation of the prototype.

The average temperature in the first week of start-up was 16 °C, the stream flow was 5000 m³h⁻¹ and was mixed with clean air (H₂S loads >50 gH₂Sm⁻³h⁻¹).

Process operation and monitoring. The test phase lasted 6 months and is still ongoing. The aim of this preliminary test period was to evaluate the suitability of biodisc rotation to control biomass removal. The goal is obtain a better understanding of the behaviour of the system relating to parameters variation and, at a later stage, to model it.

Biodiscs rotation. The experimental plan was designed to test different rotation speeds and to study the effect of the intermittent rotation. Gap time tested: 1, 5, 15, 60, 90, 180, 240, 720 minutes and more. The velocity range tested was from 0.1 to 3 rpm.

Temperature. The prototype was used in two different seasons, keeping constant the other operating parameters, to assess the effect of temperature to the kinetics of the process.

Recirculation flow rate. The flow rate was varied (3-10 m³h⁻¹) and has also been tested intermittent recirculation.

pH setpoint. The pH setpoint was gradually varied from 3 to 6.5.

The monitoring of the prototype included the analysis of biological, chemical and physical parameters. Probes were installed to measure the pH, suspended solids and dissolved ones and the relative flow gas. A Gas Chromatograph (Agilent 7890B) equipped with Flame Photometric Detector measures the concentrations of H₂S in the influent and effluent. In the recirculation liquid the following parameters were measured: COD, SCOD, TOC, Ammonium, phosphate. Biodiscs and recirculation water were sampled for the characterization of biomass twice a week. The respirometric and titrimetric analyses were carried out using an open respirometer (named MARTINA and produced by Spes Srl, Italy).

RESULTS AND DISCUSSION

The H₂S loads incoming were every variables in the seasons and during the day; this aspect is an important factor to take into account. The prototype dampens part of the oscillations. After the inoculum we observed, as shown in figure 1, an increase in the removal capacity.

![Figure 1](image.png)

**Figure 1.** The increase of the removal capacity during the start up

The MBBTF received no H₂S loads throughout August. The MBBTF started again in September, but as shown in figure 2, the removal capacity growth quickly enough and there was no need of further inoculum.
Figure 2. The growth of the removal capacity at September

Temperature was shown to be an important aspect influencing the removal capacity and efficiency, as shown in figure 3. There is no temperature control system in the prototype and is dependent from external temperature.

Figure 3. The prototype temperature and the removal capacity

The pH control system plays an important role because the biomass works better at constant pH. A better removal was observed at acid pH as shown in figure 4. The pH setpoint was gradually from 3 to 6.5 to favour H$_2$S transfer from gas to liquid phase. Further investigations are in progress to investigate this aspect and evaluate the variation in microbial composition at varying pH.

Figure 4. The prototype temperature and the removal capacity (20-27 °C)

The intermittent rotation is able, with loads and flow experienced, to remove the excess biomass;
the rotation continuous or very frequent cleans thoroughly biodiscs. We observed that 0.3 revolutions per minute is an enough speed for removal. The intermittent flow, with loads and flow experienced, is not the ideal configuration for the proper humidification of the bed (this aspect is dependent also to the rotation and air flow). The effect of recirculation on the posting of biomass is lower than the rotation. The recirculation flow rate influenced the change in pH during procedure make up. The prototype to maintain the pH setpoint consumes 3 m$^3$ of water (alkalinity 700 mg l$^{-1}$ CaCO$_3$) for kg H$_2$S removed. The preliminary tests with respirometric techniques, on the biomass taken from the prototype and executed at pH setpoint 3, shown an endogenous decay of 0.4 d$^{-1}$, but further estimates with respirometric and titrimetric (at pH 3) are still ongoing.

**CONCLUSIONS**

The removal efficiency was measured on average higher than 80%, the upper measured value of removal capacity was 90 gH$_2$S m$^{-3}$h$^{-1}$. The accumulation of biomass in the bed is controllable by rotation of the discs at a low speed and, consequently, the pressure drop between inlet and outlet were found to be very low (1-3 mbar). These results suggest that the limits of the technology have not yet been achieved; in the coming months will be tested new strategies and more high loads of H$_2$S.

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