

Effects of CO₂ and methanol on the degradation of hydrogen sulfide in a biotrickling filter

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ABSTRACT. In this study, the effects of CO₂ and methanol on the performance of a biotrickling filter (BTF) packed with plastic Pall rings and treating a H₂S-polluted waste gas were investigated to establish the optimum operating conditions and design criteria. The CO₂ concentration had no effect on the biodegradation at H₂S concentrations below 50 ppm. In the range of 50-127 ppm H₂S, CO₂ concentrations between 865-1087 ppm enhanced H₂S removal, while higher concentrations of 1309-4009 ppm CO₂ slightly inhibited H₂S removal. However, the methanol concentration had a negative effect on the bioreactor's performance. In the range of 0-81 ppm methanol, the maximum elimination capacity of H₂S dropped from 23.82 to 6.42 g H₂S.m⁻³.h⁻¹ after adding that carbon source.

1 INTRODUCTION

Hydrogen sulfide (H₂S) is a toxic, colorless, flammable gas heavier than air, with an odor threshold of about 0.47 ppb. It is released to the atmosphere as a by-product of industrial processes including, among others, sour gas flaring, petroleum refining, wastewater treatment, food processing, and pulp and paper manufacturing. The removal of H₂S from waste gases is necessary because it is harmful for living organisms, *i.e.* its MAC value is 10 ppm, it has a low odor threshold concentration, and it contributes to the deterioration of the environment. Furthermore, the oxidation products of H₂S, namely SO₂ and SO₃, are considered to be major contributors to acid rain. Therefore, strict regulations are necessary for controlling the emission levels. A host of methods has been developed to purify gas streams containing H₂S. Compared with physical and chemical processes, such as activated carbon adsorption, ozone oxidation, incineration, and scrubbing, biofiltration is considered economical, cleaner and greener because of its low operation costs, absence of residuals, and emission of no NO_x and quite less CO₂ than thermal oxidation. Biofiltration is a promising technology involving the flow of a polluted air stream through a bed of porous media supporting biological growth on volatile compounds. Under optimal conditions, biodegradable contaminants are rapidly converted to harmless end-products without the accumulation of intermediates or dead-end metabolites. Thus, biofiltration is a viable and cost-effective alternative to

conventional technologies for the treatment of low-concentration polluted air streams (Devinny *et al.*, 1999; Kennes and Thalasso, 1998; Kennes and Veiga, 2001).

The biological removal of H₂S has been studied by a number of researchers, mainly under heterotrophic conditions in presence of organic carbon substrates (Jin *et al.*, 2005a). However, hardly any reports have been published on the autotrophic removal of H₂S from polluted air, nor on the effects of process conditions as CO₂ concentration on its efficiency. The heterotrophic removal of H₂S from polluted air requires the presence of an external organic carbon source which may sometimes be available, for example when treating waste air from wastewater treatment plants and using such wastewater as trickling phase. Nevertheless, whenever an external carbon source is not directly available, the autotrophic removal of H₂S will be cheaper and more advantageous since it is based on the use of CO₂ from air as a carbon source. Another advantage of fomenting the activity of autotrophic rather than heterotrophic biocatalysts is that the slower biomass growth and build-up of the former will avoid clogging problems, quite typical in heterotrophic systems. Autotrophs are also interesting because of their low nutritional requirements. It is interesting to note that autotrophic microorganisms do not produce any CO₂ as happens with heterotrophs. Since they fix CO₂ during the removal of H₂S, the CO₂ concentration could presumably have an influence on the biodegradation rate of H₂S and the bacteria's growth rate. H₂S and CO₂ may coexist in a variety of polluted gas streams, *e.g.* pressurized natural gas, synthesis gas, biogas, as well as polluted air released from wastewater treatment plants, pulp and paper industries, or refineries. Different authors (Haddadin *et al.*, 1993; Torma *et al.*, 1972) mentioned the influence of carbon dioxide on bacterial growth, biomass concentration as well as on the rate of sulfide oxidation. They suggest that the CO₂ concentration may play an important role in sulfide biooxidation. Therefore, the effect of CO₂ on the removal efficiency of H₂S may provide important information to develop efficient biotechnological processes for field application.

To date, most lab-scale biofiltration studies address the removal of single pollutants under constant operating conditions. Such conditions are highly unusual at wastewater treatment plants and other facilities. For instance, the waste gas of paper and pulp industry is a complex mixture of H₂S and other reduced sulfur compounds (such as dimethyl sulfide, dimethyl disulfide, and methyl mercaptan), as well as volatile organic compounds (such as methanol, terpenes, alcohols, phenol, ketones, and formaldehyde).

The actual composition and individual concentrations often vary substantially over time. Since the co-treatment of H₂S and VOCs in biotrickling filters is a relatively unexplored area, and autotrophic microorganisms do not use methanol (CH₃OH) as a carbon source for growth, the simultaneous biotreatment of H₂S and CH₃OH was investigated in this study. H₂S and methanol are two major air pollutants of industries such as the pulp and paper industries. CH₃OH is a volatile organic compound commonly used in industry, which may have harmful effects on human health. Therefore, it has been listed as one of the 189 Hazardous Air Pollutants included in the 1990 Clean Air Amendment list in the US. Even though it may also have negative effects on microorganisms, different studies have proved that methanol can effectively be removed at rates up to 280 g.m⁻³.h⁻¹ from air by means of bioreactors (Prado *et al.*, 2005).

The objective of this study is to assess the impact of CO₂, and the cotreatment of waste gases containing a mixture of H₂S and CH₃OH in an autotrophic biotrickling filter.

2 MATERIALS AND METHODS

2.1 Microorganisms and cultivation

An autotrophic H₂S-degrading culture obtained from the activated sludge of the full-scale wastewater treatment plant of a resin-producing industry was enriched in a biofilter. The characteristics of the sludge have been described elsewhere (Prado *et al.*, 2004). The biomass was acclimated to sulfur compounds in a sodium thiosulphate mineral medium without addition of any external organic carbon source. The composition of the liquid medium used was (in g.l⁻¹): KH₂PO₄, 2; K₂HPO₄, 2; NH₄Cl, 0.4; MgCl₂.6H₂O, 0.2; FeSO₄.7H₂O, 0.01; and Na₂S₂O₃.5H₂O, 8 (Jin *et al.*, 2005a).

2.2 Experimental setup

The schematic of the biotrickling filter used in this study is shown in Figure 1 and has been described previously in detail (Jin *et al.*, 2005a). It is a cylindrical packed bed reactor made of glass, 75 mm in diameter and 700 mm in height. The packed column was filled with polypropylene Pall rings of a nominal height of 15 mm. The total height of the packed bed was 640 mm. The Pall ring bed had an initial porosity of 91% and a specific surface area of 350 m².m⁻³. The glass column contained four equidistant sampling ports. All fittings, connections and tubings were made of Teflon. H₂S was introduced by passing the air stream over a H₂SO₄ solution into which a solution of Na₂S was dripped. Gas phase H₂S concentrations ranging from 0 to 190 ppm were obtained by changing the Na₂S concentration and/or dripping rate. The resulting synthetic waste gas was introduced through the bottom of the column for counter-current flow operation. Initially, the gas flow rate was maintained constant at 7 L.min⁻¹, corresponding to an empty bed residence time of 24 s. The aqueous mineral medium described above, without Na₂S₂O₃ nor any external carbon source, was continuously recirculated over the packed bed using a peristaltic pump (model 323E/D, Watson-Marlow Limited, Falmouth Cornwall, England) at a constant volumetric flow rate of 2.77 L.h⁻¹. The nutrient solution of the biotrickling filter was renewed every day. During the experimental study on the effect of CO₂, carbon dioxide from a gas cylinder flew first through a pressure gauge (RBDE-30/PS-3.5, Carbueros Metalicos S.A., La Coruña, Spain) and then through a flowmeter (Model VCD 1000 flow controller, Porter Instrument Co., Inc., Hatfield, PA, USA) in order to reach the expected CO₂ concentration in the inlet gas. During the experiment on the CH₃OH effect, CH₃OH was

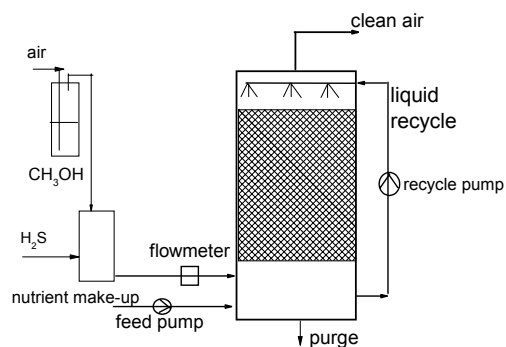


Figure 1. Schematic of the laboratory scale biotrickling filter.

introduced into the gas stream by feeding a side air stream through a bottle filled with pure CH_3OH (Figure 1).

2.3 Analytical methods

Inlet and outlet H_2S concentrations were determined using a gas sensor (Dräger Sensor XSEC H_2S HC6809180). Methanol concentration was measured by means of a HP-6890 gas chromatograph (Agilent T., Spain) equipped with a 30 m \times 0.53 mm HP-PLOT Q column and a flame ionization detector, operating in splitless mode. Oven temperature was 130 °C, while both the injector and detector temperature was 150 °C. Samples were injected using a 2.5 cm³ gas-tight Hamilton syringe. Under these conditions, the retention time of methanol was 3.5 min (Prado *et al.*, 2005). Similarly, CO_2 concentrations were measured on another Hewlett-Packard 5890 series II GC equipped with a thermal conductivity detector (TCD). The CO_2 concentrations were determined at an injection temperature of 90 °C, an oven temperature of 25 °C and using a TCD at 100 °C.

3 RESULTS AND DISCUSSION

3.1 Influence of CO_2 on performance

In this experiment a biotrickling filter was fed H_2S -polluted air enriched with different CO_2 concentrations.

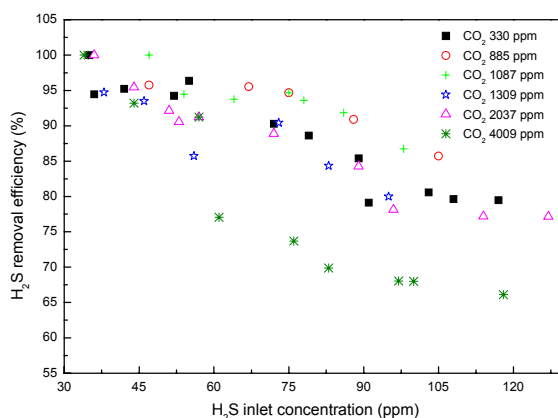


Figure 2. Effect of the CO_2 concentration on H_2S removal.

According to the data shown in Figure 2, it appeared that in the lower range of H_2S concentrations, *i.e.* <50 ppm, the CO_2 concentration had no visible effect on the removal efficiency of H_2S . However, a non-negligible enhancement of H_2S removal was found when gradually increasing the content of CO_2 to 4009 ppm, at H_2S concentrations higher than 50 ppm. This indicated that at lower H_2S concentrations, the inherent CO_2 in the waste gas did not limit the degradation rate, but at high H_2S concentrations the pollutant's removal rate was limited by the availability of CO_2 , probably due to the mass transfer rate of CO_2 from the gas phase to the liquid/biofilm. When the CO_2 concentration was slightly increased from 865 ppm to 1087 ppm, no detectable

difference in H₂S removal was observed. However, the removal efficiency decreased as the CO₂ concentration was further increased to 1309 ppm or more. This means that higher CO₂ concentrations can enhance the removal of H₂S at CO₂ concentrations ranging between ambient levels and 1087 ppm. However, higher concentrations of CO₂, e.g. >1309 ppm, did not further improve the degradation of H₂S.

3.2 Addition of methanol to a H₂S-degrading biotrickling filter

Methanol was deliberately supplied in the range of 18 to 81 ppm to allow for the determination of a possible effect (positive or negative) of a carbon source as CH₃OH on H₂S removal in an originally autotrophic system.

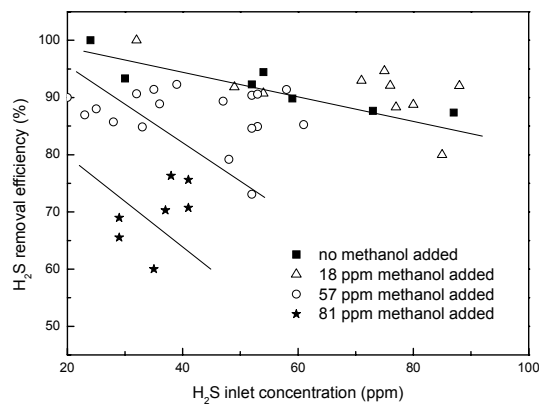


Figure 3. Influence of methanol on the performance of a biotrickling filter removing H₂S.

Figure 3 shows that the removal of H₂S was not affected by the addition of 18 ppm of CH₃OH. When the CH₃OH concentration was increased above this value, from 18 to 81 ppm, a gradual decrease in removal efficiency of H₂S was observed as the gas

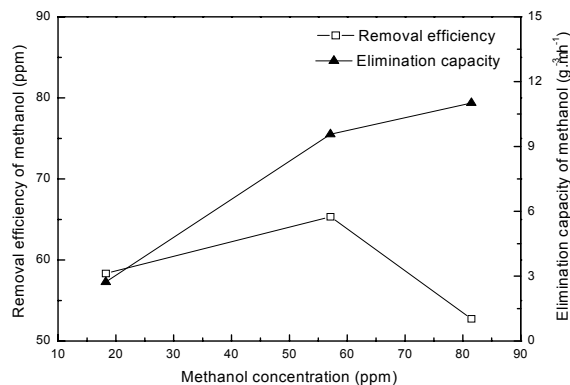


Figure 4. Removal efficiency and elimination capacity of CH₃OH.

concentrations of CH₃OH increased. The maximum elimination capacity of H₂S dropped from 23.82 to 6.42 g H₂S.m⁻³.h⁻¹. This resulted probably to the fact that autotrophic microorganisms were originally dominated in the biofilter, and that they use CO₂ as carbon source instead of CH₃OH for H₂S removal. The presence of CH₃OH caused a decrease of the autotrophic activity.

Conversely, the elimination capacity of CH₃OH did gradually increase from 2.73 to 11 g m⁻³.h⁻¹ during the same period (Figure 4). This value is much smaller than the maximum elimination capacities reported in the literature, which range from 50-250 g.m⁻³.h⁻¹ (Sologar *et al.*, 2003). This probably resulted from the pH of the biofilter, around 2, that was not optimum for methanol degradation. The general optimum pH for VOCs degrading microorganisms is usually around 7. On the other hand, only H₂S was fed at the beginning and hardly any methanol biodegrading microorganisms were present, which is another reason to explain this phenomenon. The addition of CH₃OH allowed the growth of heterotrophs which utilize methanol as carbon source. The removal efficiency of CH₃OH did first increase from 58% to 65% and then decreased to 52% at inlet concentrations of CH₃OH of 18, 57, and 81 ppm, respectively.

4 CONCLUSIONS

The following conclusions can be drawn from the results presented in this study:

(1) The CO₂ concentration has no significant effect on the BTF's performance in the low range of H₂S concentrations, *i.e.*, < 50 ppm. When the H₂S concentration is increased above this level, the CO₂ concentration seems to improve the BTF's performance at moderate CO₂ concentrations, below 1309 ppm.

(2) The introduction of CH₃OH had no significant influence on H₂S removal when the inlet concentration of CH₃OH was below 18 ppm. In the range of 57-81 ppm methanol, the removal of H₂S was inhibited by the presence of CH₃OH. The maximum elimination capacity of H₂S dropped from 23.82 to 6.42 g H₂S.m⁻³.h⁻¹.

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