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Removal of Pollutants from the Air in a Copper-Ore Mine Using a Compact Trickle-Bed Bioreactor

Damian Kasperczyk*[a], Krzysztof Urbaniec[b], Krzysztof Barbusinski[c]

[a]Ekoinwentyka Ltd., Szyb Walenty 26, 41-707 Ruda Śląska, Poland
[b]Warsaw University of Technology, Plock Branch, Jachowicza 2/4, 09-402 Plock, Poland
[c]Institute of Water and Wastewater Engng, Silesian University of Technology, Konarskiego 18, 44-100 Gliwice, Poland
biuro@ekoinwentyka.pl

Selected results are presented of an on-going project conducted by Ekoinwentyka Ltd. with the aim to design, test and apply a compact trickle-bed bioreactor to the biodegradation of H_2S and VOC mixture present in the air in a copper-ore mine at a depth of 1,000 m underground. The experiments were performed using a semi-industrial scale bioreactor in which gas and liquid phases flowed co-currently in downward direction through a bed made of polyethylene rings. The bioreactor was inoculated with a co-culture of microorganisms developed by Ekoinwentyka Ltd. especially for the chosen pollutants and bacterial strains found in the cooper-ore mine. During the period of test operation of the bioreactor in a mine corridor, it was found that pollutant concentration in the air was normally moderate but temporary bursts of very high H_2S concentration were also observed. An increase in H_2S concentration to 40 – 60 ppm usually caused a drop in biodegradation efficiency but once the concentration returned to its normal range below 38 ppm, stable process conditions were restored quickly. Despite harsh working conditions that are characteristic of the copper-ore mine 1000 m deep, the experimental set-up has been operated reliably for several weeks and a satisfactory level of the efficiency of pollutant removal (the factor of H_2S conversion typically in the range 80 – 100 % and that of VOC conversion 90 – 100 %) has been achieved.

1. Introduction

Hydrogen sulfide (H_2S) and volatile organic compounds (VOCs) belong to the most harmful atmospheric pollutants. H_2S has an unpleaseant odor and is known to have adverse health effects even at a very low concentration in air (Partti-Pellinen et al., 1996). Certain VOCs like styrene and its metabolites are known to have serious negative effects on human health (Vodicka et al., 2006). Apart from being toxic and cancerogenic, they contribute to the forming of tropospheric ozone and photochemical smog, and exhibit a high global warming potential. Industrial emissions of H_2S and VOCs − coming from such sources as chemical and petrochemical plants, pulp and paper industries, deep and open-pit mines, etc. − are subject to increasingly stringent environmental regulations and require efficient abatement measures. Among a number of pollutant removal technologies that are available for treating the polluted air streams, the biological treatment method is particularly interesting as it is based on the natural ability of microorganisms to degrade pollutants, and it does not shift the pollution problem from air to other environmental compartments, that is, to water or soil (Diks and Ottengraf, 1991). Although applications of bioprocess engineering to waste management are relatively new, the industries have recognized important advantages of pollutant biodegradation such as mild process conditions including low values of pressure and temperature, absence of the explosion risk, and safety for people and environment. It has also been reported that investment and operating costs of biodegradation may be lower than those of the chemical methods of pollutant abatement (Alonso et al., 1999).
Regarding the removal of single pollutants from contaminated air in biofilters using various microorganisms, a number of studies are available in the literature. H_2S removal from air has been studied by Ramirez et al., (2009); publications on H_2S removal from various gas streams are listed in review

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papers by Syed et al. (2006) and more recently by Rattanapan and Ounsaneha (2012). Among VOCs, biodegradation of polyalkylated benzenes was studied by Hekmat and Vortmeyer (1994), toluene removal by Cox et al. (2000), phenol elimination by Sa and Boaventura (2001), biodegradation of vinyl acetate by Kasperczyk and Bartelmus (2010), and removal of styrene – by Moon et al. (2010). Interestingly, styrene can be biodegraded by various microorganisms as indicated by the research results of Hwang et al. (2008) who used *Brevibacillus sp.* and those of Kasperczyk et al. (2012) who experimented with *Pseudomonas sp*. Some experimental data are also available on the removal of pollutant mixtures from air in compact trickle-bed bioreactors (CTBB) continuously fed with liquid media. Biodegradation of mixtures of aromatic hydrocarbons was studied by Hekmat and Vortmeyer (2004) and mixtures of VOCs and vicinal compounds − by López et al. (2013). Cox and Deshusses (2001) investigated biodegradation of H_2S mixed with toluene and Jin et al. (2007) − H_2S mixed with methanol.
The present study is based on the experimental results of an on-going project conducted by Ekoinwentyka Ltd. with the aim to design, test and apply a compact trickle-bed bioreactor, fed continuously with mineral salt solution, to the biodegradation of pollutants contained in the air in a copper-ore mine at a depth of 1000 m underground. In an earlier publication by two of the present authors (Kasperczyk and Urbaniec, 2013), the focus was on VOC degradation and some preliminary data on H_2S abatement were presented. The present paper is concerned mainly with the degradation of hydrogen sulfide. The aim of the experiments was to determine the ranges of parameters of reactor operation at which the tested microorganisms are most effective at H_2S degrading. Consequences of fatal pollutant overload such as the time required for subsequent regeneration of the microorganisms and returning to stable process conditions, were also studied.

2. Materials and methods

The principle of biotrickling filtration is schematically shown in Figure 1. In a biotrickling filter, contaminated air is forced through a packed bed, either downflow or upflow and a liquid – typically an aqueous solution of mineral salts − is simultaneously recycled over the packing. The packed bed, usually made of an inert material, provides the necessary surface for biofilm attachment and for gas-liquid contact. The liquid provides moisture, nutrients to the process culture and a means of controlling pH or other operating parameters.
The experiments were performed using a semi-industrial scale CTBB bioreactor with a working volume of 74 dm^3 which was developed by modifying the apparatus used in earlier work (Kasperczyk and Urbaniec, 2013). The bioreactor vessel with a total height of 2.1 m consisted of three segments made of 304 stainless steel selected to withstand harsh working conditions and corrosive atmosphere that are characteristic of the mine 1,000 m deep. Inside the vessel, gas and liquid phases flowed co-currently in downward direction through a bed of 15×15 mm polyethylene rings. During the experiments, the height of the bed was varied between 0.7 and 1.0 m.
The bioreactor was inoculated with a co-culture of microorganisms including bacterial strains developed by Ekoinwentyka Ltd. especially for application in the copper-ore mine and other microorganisms found in the mine, both at the ground level and in the underground corridors.

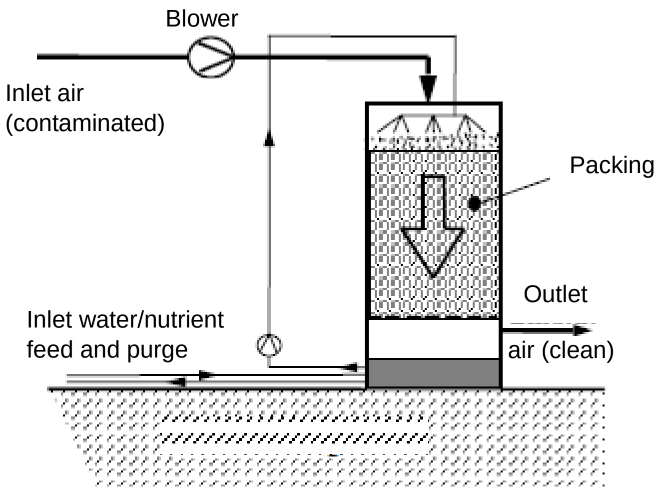

Figure 1: Operating principle of biotrickling filtration in a compact bioreactor (after Deshusses et al., 2003)

Figure 2: Experimental setup including the bioreactor and cabinet with controls and measuring equipment. Not shown: computer-assisted data logging system

A photo of the experimental setup is shown in Figure 2. It was operated maintaining the temperature and pH within their ranges identified as most suitable for the used microorganisms, that is, t = 303 ± 7 K, and pH = 5.0 - 7.5. The recirculation rate of the liquid medium was maintained in the range 1.0 to 2.0 m^3h^{-1} whereas the gas flow rate was varied between 2.0 and 20.0 m^3h^{-1}.
During the experiments, the concentration of pollutants in the gas phase both at the inlet and outlet of the bioreactor was measured using Varian Star 3,400 chromatograph by Varian Associates and industrial meters: MiniRAE 2000 and MultiRAE by RAE Systems, Ventis MX4 by Industrial Scientific, and H2S Gas Detector by Draeger. The detailed qualitative analysis of microorganisms in the recirculating liquid medium was performed using NEFERM Test by Lachema a.s., whereas the quantitative analysis of bacteria suspension was performed by means of spectrophotometric methods and continuously, using SOLITAX inline probe by Hach Lange.

3. Results and discussion

After starting up the experimental pollutant biodegradation system at its test location in the mine corridor, the procedure of immobilization of microorganisms in the bioreactor bed was carried out. Maintaining the recirculation rate of the liquid at its minimum, the microflora was allowed to grow on the packing material during a period of four days. After that, regular measurements of H_2S and VOC concentration in the mine air and at the bioreactor outlet were started and the test operation continued for a period of about a month.
For each pollutant, the efficiency of biodegradation was expressed by the conversion factor according to the formula:

$$K = 100 \cdot (C_{gi} - C_{go})/C_{gi} \ [\%] \quad (1)$$

where C_{gi} denotes concentration of the pollutant in the air at bioreactor inlet, and C_{go} – concentration at bioreactor outlet.

3.1 Initial experience of bioreactor operation

In Figure 3, the results of biodegradation of hydrogen sulfide recorded on days 3 and 4 of test operation are plotted. As can be seen, H_2S concentration in the mine air, that is, at the bioreactor inlet varied between 12 and 58 ppmv. H_2S concentration in the air at bioreactor outlet oscillated between 0 and 22 ppmv and the resulting efficiency of H_2S biodegradation was in the range 60 – 100 %.

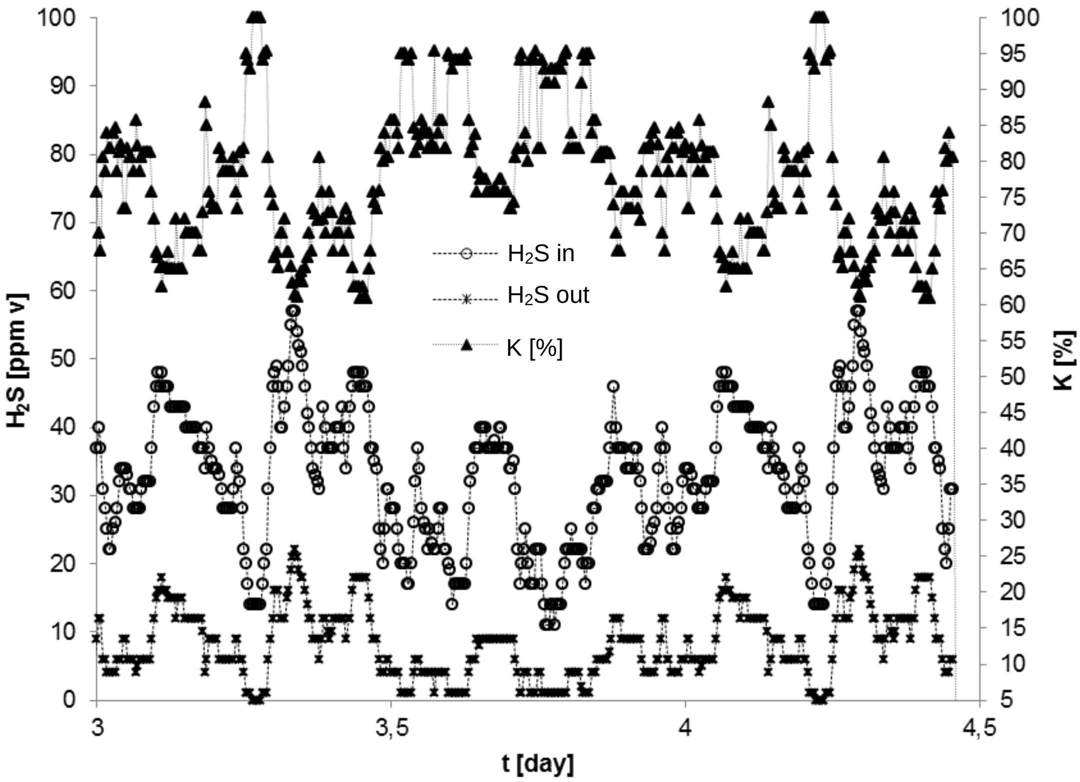

Figure 3: H_2S concentration at bioreactor inlet and outlet, and H_2S conversion factor recorded on measurements days 3 and 4

In the middle of day 4, the computer-assisted data logging was interrupted due to equipment failure caused by high temperature and high humidity of the air but bioreactor operation was continued and so were H_2S measurements using Draeger H_2S Gas Detector. On day 5, H_2S concentrations in the mine air and at the bioreactor outlet were 36 ppm and 6 ppm, respectively; the average conversion factor was about 83 %.

A serious disturbance in bioreactor operation occurred starting day 9. As a consequence of rock blasting operations carried out in the mine, power supply to the biodegradation system was broken and the computer-assisted data logging was interupted again. The power supply could not be resumed for a two-day period during which the liquid medium had not been recirculated thus cutting off the supply of nutrients to the microorganisms in the bioreactor bed. However, after returning to normal system operation on day 11 it turned out that the microorganisms survived and their biodegradation capability could be restored quickly. On day 12, while the computer-assisted data logging system still was inoperative, H_2S concentrations were measured using Draeger H_2S Gas Detector and found at 27 ppm in the mine air and 2 ppm at the bioreactor outlet, that is, the conversion factor was about 92 %.

It is worth mentioning that system robustness was additionally confirmed by its response to longer periods – lasting for up to 10 h − of H_2S concentration increased to 45 – 60 ppm, on days 2 and 7. No serious poisoning of microorganisms was observed as the conversion factor remained in the range 60 – 80 % and later, when H_2S concentration was decreased below 40 ppm, quickly returned to a level above 90 %.

3.2 Investigation of stable bioreactor operation

Having restored normal operation of the biodegradation setup and restarted the data logging system, it was possible to carry out the remaining part of the experimental programme without further problems. A sample of results of the biodegradation of hydrogen sulfide is shown in Figure 4. As can be seen, at H_2S concentration in the mine air 10 – 38 ppm the conversion factor is in the range 80 – 99 %. When the concentration is increased to 40 – 50 %, the conversion factor drops to 60 – 80 %. It can be interpreted as an indication of flexibility of the biodegradation system that despite a 5-fold increase in H_2S concentration compared to its lowest value, the conversion factor is reduced by not more than about 1/3.

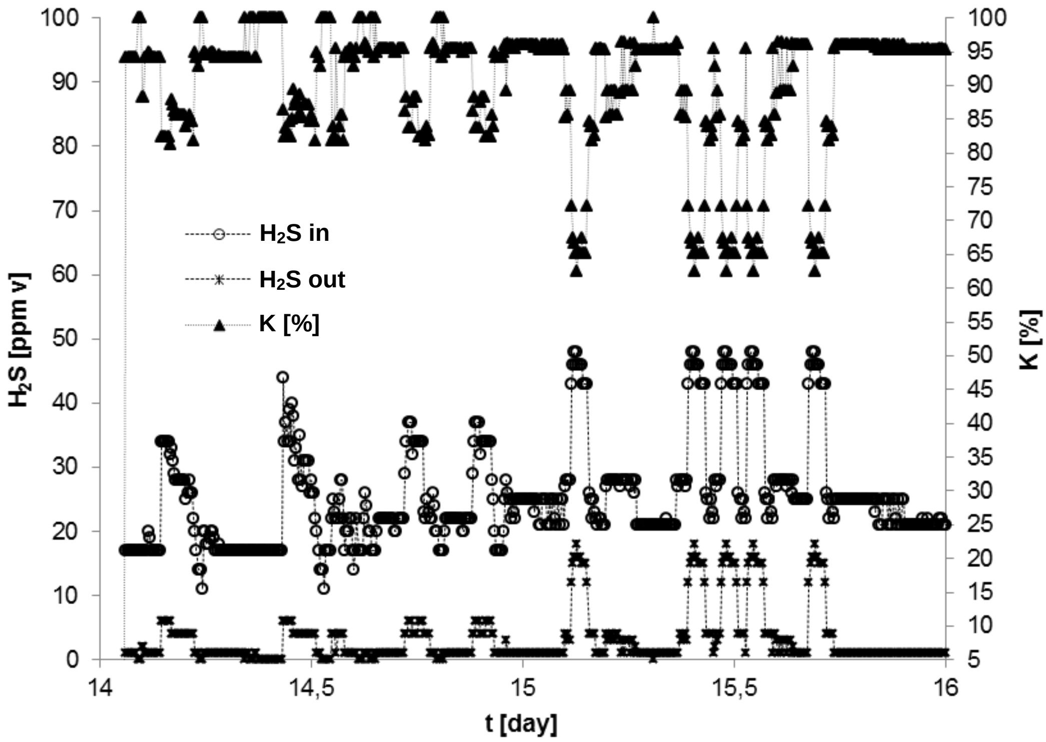

Figure 4: H_2S concentration at bioreactor inlet and outlet, and H_2S conversion factor recorded on measurement days 14 and 15

It is important to note that in parallel to hydrogen sulfide measurements, the biodegradation of VOCs was also monitored. At VOC concentration below 70 ppm, the VOC conversion factor was maintained in the range 90 −100 % thus confirming VOC biodegradation results previously reported by Kasperczyk and Urbaniec (2013).

4. Conclusions

During the test operation of the pollutant biodegradation system featuring CTBB bioreactor in the copper-ore mine, the ranges of H_2S and VOC concentration that are characteristic of the air in mine corridors were determined. The difficulties experienced during the initial period of system operation made it possible to identify the requirements of system robustness necessary to withstand the influence of the harsh conditions of the deep-mine environment including by-effects of the use of explosives in mining operations.
The experience gathered during the test period proved that the co-culture of microorganisms selected for H_2S and VOC degradation performed satisfactorily and was able to survive both frequent bursts of increased concentration of pollutants and an unexpected disturbance in the nutrient supply.
For most of the time of test operation, H_2S concentration in the mine air was below 38 ppm and H_2S conversion factor was in the range 80 – 99 %; in the periods of concentration increased to 40 – 50 %, the conversion factor typically dropped to 60 – 80 %. VOC concentration in the air was normally below 70 ppm and VOC conversion factor was maintained in the range 90 −100 %.
Summing up, the efficiency of H_2S and VOC biodegradation proved to be satisfactory thus confirming the suitability of biodegradation as a method for improving the quality of air in the mine corridors where the presence of personnel is required. The measurement results and experience gathered constitute a convenient basis for process upscaling and planning of an industrial-scale pollutant degradation system.

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