Journal of Zhejiang University SCIENCE B
ISSN 1673-1581 (Print); ISSN 1862-1783 (Online)
www.zju.edu.cn/jzus; www.springerlink.com
E-mail: jzus@zju.edu.cn

Performance of biotrickling filters for hydrogen sulfide removal under starvation and shock loads conditions*

Lan-he ZHANG†[1,2], Xiu-li MENG[1], Ying WANG[1], Li-dan LIU[1]

([1]*School of Chemical Engineering, Northeast Dianli University, Jilin 132012, China*)

([2]*Department of Environmental Science and Technology, Harbin Institute of Technology, Harbin 150090, China*)

†E-mail: zhanglanhe@163.com

Received Mar. 1, 2009; Revision accepted July 1, 2009; Crosschecked July 7, 2009

Abstract: In the industrial operation of biotrickling filters for hydrogen sulfide (H_2S) removal, shock loads or starvation was common due to process variations or equipment malfunctions. In this study, effects of starvation and shock loads on the performance of biotrickling filters for H_2S removal were investigated. Four experiments were conducted to evaluate the changes of biomass and viable bacteria numbers in the biotrickling filters during a 24-d starvation. Compared to biomass, viable bacteria numbers decreased significantly during the starvation, especially when airflow was maintained in the absence of spray liquid. During the subsequent re-acclimation, all the bioreactors could resume high removal efficiencies within 4 d regardless of the previous starvation conditions. The results show that the re-acclimation time, in the case of biotrickling filters for H_2S removal, is mainly controlled by viable H_2S oxidizing bacteria numbers. On the other hand, the biotrickling filters can protect against shock loads in inlet fluctuating H_2S concentration after resuming normal operation. When the biotrickling filters were supplied with H_2S at an input of lower than 1700 mg/m^3, their removal efficiencies were nearly 98% regardless of previous H_2S input.

Key words: Biotrickling filter, Starvation, Shock loads, Odor, Hydrogen sulfide
doi:10.1631/jzus.B0920064 **Document code:** A **CLC number:** X512

INTRODUCTION

Odor mainly composed of hydrogen sulfide (H_2S) from the pharmaceutical wastewater treatment plant is one of the major public perception nuisance problems in the pharmaceutical industry. The removal of malodorous H_2S has been traditionally accomplished by using physical or chemical technologies, such as vapor scrubbing, incineration, or adsorption (Bouzaza *et al*., 2004; Le Leuch *et al*., 2003; Lee *et al*., 1999; Bandosz, 2002). Nevertheless, these technologies are usually uneconomical because they only transfer waste gases from the gas phase to another phase that either requires the use of further treatments or is expensive to maintain good operation performance. Currently, biological purification technology has become an important alternative to many conventional methods, especially for odor associated with readily biodegradable compounds (Jiang *et al*., 2009; Potivichayanon *et al*., 2006; Liu *et al*., 2005; Jin *et al*., 2007). The low operating cost attributes to the utilization of microbial oxidation at ambient conditions instead of thermal or chemical oxidation conditions. Under proper operation, biological process is highly efficient and environmentally friendly. The most widely utilized bioreactors for air pollution control are biofilters and biotrickling filters. Biotrickling filter functions by passing the contaminated air stream through a moist bed of permeable material, on which liquid biofilms are formed. A biotrickling filter is, in fact, a three-phase biocatalytic oxidizer and is essentially made from a support carrier on which

* Project supported by the Foundation for Society Development of Jilin Province (No. 20080412-1), the Education Research Foundation for Science and Technology Development of Jilin Province, and the Foundation for Doctor Research in Northeast Dianli University of Jilin Province (No. BSJXM-200710), China

microorganisms are able to grow when optimal conditions are provided. Thus contaminants are induced to diffuse from the gaseous phase through the wet biofilm and are consequently catabolized aerobically to carbon dioxide, water vapor, and/or inorganic salts.

Performance of biotrickling filter is usually studied under relatively steady-state operation conditions in laboratory systems. Owing to the variable industrial schedules, pilot-scale or full-scale biotrickling filters are usually exposed to many perturbations as a result of fluctuation or discontinuous shock loads. For instance, periodic interruptions in contaminant discharge and/or process condition changes may lead to fluctuating shock loads. Interruptions are also common phenomena in the industrial operation when plants are periodically shut down or during equipment malfunctions and equipment repair period. Periods of interruption may vary from a few minutes, as for lunch breaks, to several days. Thus operational problems normally ignored in the laboratory systems appear, and resuming normal operation is vital after encountering variable operation conditions. It is important to investigate the performances of biotrickling filter in the absence of pollutant feed and during the time when shock loads take place.

Only a few studies discussed the effects of starvation and shock loads on the performances of biofilters for H_2S removal. Wani *et al*.(1998) described the performance of the biofilters with different filter carriers under periods of starvation and fluctuating H_2S concentration conditions. Cox and Deshusses (2002) designed two identical biotrickling filters, one operated at pH 4.5 and the other at pH 7.0, to treat mixed gas containing H_2S and toluene under fluctuating H_2S and toluene concentrations. Hartikainen *et al*.(2002) investigated the effect of fluctuating H_2S concentration on the removal efficiency of biofilter and found that low H_2S concentration was mainly produced in a wastewater pumping station. However, in most cases, inlet concentrations and volumetric loads of H_2S were relatively low and thus shock loads were also relatively mild. Little is known on the starvation experiments of biotrickling filter for H_2S removal and a limited number of studies involved actual measurements of biomass and viable bacteria numbers during starvation. For practical operation considerations, it is important to obtain reliable data on the behaviors of biotrickling filters during long starvation and shock loads periods. The present research described the results of a bench-scale study investigating the effects of H_2S starvation and shock loads on biotrickling filter performances. Interruption of H_2S feed was achieved under selected conditions (with or without air flow, with or without spray liquid supply) for a duration from 21 to 45 d. Responses to shock loads after starvation experiment were also discussed under continuous fluctuation concentration conditions.

MATERIALS AND METHODS

Experimental equipments and process startup

Four identical bench-scale biotrickling filters were used (Fig.1). The biotrickling filters with an inner diameter of 250 mm and a height of 1500 mm were made of transparent plexiglass tubing. In order to check the removal efficiency of H_2S at different height, each biotrickling filter was divided into three equal sections and each section was equipped with a gas sampling port. The carriers selected here were fibre balls, which have a diameter of 35 mm and a bulk density of 82 kg/m^3 without attached biomass. The void fraction of the bioreactor was 0.70. The packed carriers in each section were supported by plexiglass sieve plates. There was one port in each section of the biotrickling filter for carrier sampling and gas pressure measurement.

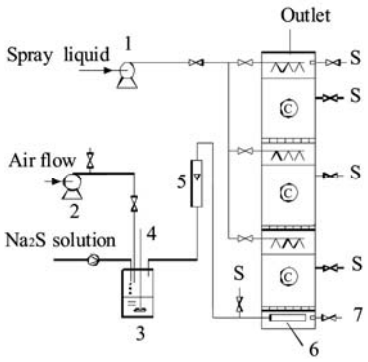

Fig.1 Schematic diagram of biotrickling filter system
1: water pump; 2: air compressor; 3: H_2SO_4 pot; 4: blender; 5: gas flow meter; 6: air distributor; 7: effluent port; C: carrier sampling ports; S: gas sampling ports

H_2S was introduced into the biotrickling filters from the bottom after flowing through the flow meter

and the treated gas exhausted from the top. Liquid from the upper reservoir tank could be sprayed regularly downward through the bioreactor by centrifugal water pump and was discharged from the bottom. The nutrient solution of spray water was as follows: KH_2PO_4, 2 g/L; $MgCl_2·6H_2O$, 0.2 g/L; K_2HPO_4, 2 g/L; NH_4Cl, 0.4 g/L; $FeSO_4·7H_2O$, 0.01 g/L.

The system was inoculated with activated sludge from pharmaceutical wastewater treatment plant, and H_2S supply concentrations were gradually increased from 3 mg/m^3 to about 120 mg/m^3 after 15 d. At the same time, fresh medium was continually added to biotrickling filter at 2 L/h of spray water flow rate and spray liquid was drained off from an effluent port. Therefore, the biofilm containing sulfur-oxidizing bacteria was gradually formed on the surface and in the pores of the carriers. Four biotrickling filters were operated similarly throughout the entire experiment, except for the starvation phase.

Starvation experiments

After a startup phase of 15 d, these 4 biotrickling filters continued to operate for additional 5 d to achieve a steady-state biomass and then were assigned to starvation experiments 1~4 (Table 1). The supply of H_2S was stopped in the biotrickling filters during the starvation experiments. In experiments 2 and 3, the spray liquid with 3 L nutrient solution was supplied every 1 h. The biotrickling filters of experiments 1 and 4 were starved without trickling liquid. Clean air supply was maintained in experiments 3 and 4, but discontinued in experiments 1 and 2.

Analytical methods

H_2S concentration was measured by gas chromatography with a flame photometric detector (Hewlett Packard 6890, 3 m×3 mm i.d. column was packed with ODTN 25% (w/v)). The dry biomass in the bioreactors was determined by regularly sampling the carrier with biofilm at same depth (35 cm). Portions of the carrier with immobilized biomass were transferred to buffer containing 1 g/L of NaH_2PO_4 and Na_2HPO_4 in a flask. The biomass was suspended by vortexing the flask for 2 min, and both the carrier and suspension with biomass were separately dried at 105 °C for 24 h.

Plate count

Samples were taken at same depth (35 cm) from the biotrickling filters described above. Samples were then put into physiological saline solution (0.9% (w/v) NaCl) with a blender in order to detach biofilm from the carrier. Dilutions of suspensions of mixed culture were plated on solid thiosulphate agar medium for enumeration of total culturable bacteria. Solid thiosulphate agar medium was made as follows: $Na_2S_2O_3·5H_2O$, 8 g/L; KH_2PO_4, 2 g/L; $MgCl_2·6H_2O$, 0.2 g/L; K_2HPO_4, 2 g/L; NH_4Cl, 0.4 g/L; $FeSO_4·7H_2O$, 0.01 g/L; Agar, 18 g/L.

RESULTS AND DISCUSSION

Performance of startup and steady state

After the biotrickling filters were inoculated, nutrient solution was added for 20 d to sustain a rapid microbial growth and to improve the degradation activity of sulfur-oxidizing bacteria before the starvation experiments. The bioreactor was acclimated by increasing the H_2S concentration gradually from 3 mg/m^3 to about 120 mg/m^3 after 15 d. Nutrient solution was supplied at 2 L/h after steady state was obtained. The airflow rate was kept at 6.5 m^3/h. Owing to the similarity of the biomass in four bioreactors, only one of the biotrickling filters was evaluated prior to the shock loads.

Fig.2 shows a rapid startup. The bioreactor achieved a steady state and the removal efficiency of H_2S kept constant after 15 d. The H_2S outlet concentration in steady state was maintained below

Table 1 Experimental design for H_2S starvation

Starvation experiment	H_2S supply	Air supply	Spray liquid with nutrient solution	Possible conditions
1	off	off	off	Equipment repair or equipment malfunction
2	off	off	on	Blower breakdown
3	off	on	on	Weekend or holiday with water supply and air kept on
4	off	on	off	Water pump malfunction

1.2 mg/m^3 and the removal efficiency of H_2S was nearly 99% with the increasing inlet concentrations. Meanwhile, a rapid accumulation of immobilized biomass was observed and there was about 0.099 g dry cell/g carrier after 15 d (Fig.3). The bioreactor could resist the shock of high loads under relatively stable biomass content at the end of acclimation phase. The increase of biomass was relatively slower compared with initial startup after 15 d, which could attribute to the fact that spray liquid could supply microorganisms with necessary nutrients and wash excess biofilm off. In the steady state phase, the experiments were conducted at a relatively high liquid trickling velocity of 5 L/h in order to avoid the clogging of the bioreactor.

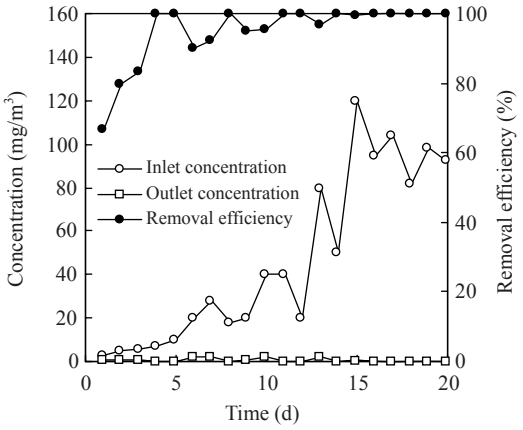

Fig.2 Continuous operation results of startup phase

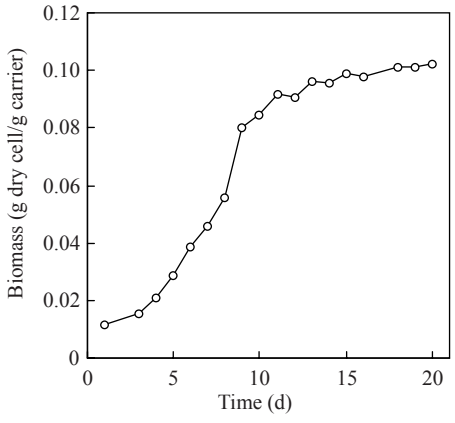

Fig.3 Increase of biomass in the biotrickling filters during the startup

Changes of biomass during the starvation

As shown in Fig.4, biomass decreased gradually in the biotrickling filters during the various types of starvation experiments. The decrease of biomass may be due to microorganism death, endogenous respiration, secondary processes such as the predation of higher organisms, and/or shear by the airflow and spray liquid. The biomass decreased slowest in experiment 1, but fastest in experiment 4. Comparing the two experiments, it is noted that airflow is an important contributing factor to the overall biomass loss because of its shear stress and oxidation capacity. Microorganism would die gradually under the aerobic and nutrient solution absence conditions. The endogenous respiration of microorganism could result in the loss of the biomass. However, it should be noted that high liquid trickling velocity could also result in biomass loss due to liquid shear stress. In the starvation experiments, liquid trickling velocity was controlled at a relatively low value (once per hour, with 3 L of nutrient solution) to supply necessary nutrient materials for microorganism and decrease the effect of liquid shear stress on the biomass.

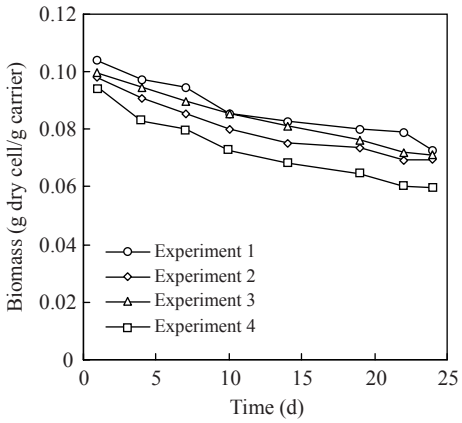

Fig.4 Decrease of biomass with the increase of starvation time

It should also be noted that a decrease in the biomass was not vital at relatively high biomass concentration. Long-term operation may result in excess biomass formation when nutrient loads and pollutant concentrations are high. Hence, periods of starvation associated with a decrease of biomass would not decrease the lifespan of the biotrickling filter. In the present experiments, the lowest biomass after starvation was about 0.06 g dry cell/g carrier after 24 d of starvation. And the biomass did not drop to a level where biodegradation efficiency would be limited during the starvation experiments. Fig.2 shows that removal efficiency of H_2S was nearly

100% when inlet concentration was 20 mg/m^3 and the biomass was nearly 0.06 g dry cell/g carrier. This indicates that H_2S removal after the starvation was related to the viable bacteria number and/or the activity of the remaining biomass.

Effect of starvation on viable bacteria numbers

Elimination capacities of H_2S have been correlated with the live microorganism count. Thus the sulfur oxidizing bacteria were enumerated during the starvation experiments.

As shown in Fig.5, the viable bacteria numbers decreased gradually in the starvation experiments. The live bacteria number decreased slowest in experiment 3 with continuous oxygen and spray liquid, but fastest in experiment 4. The results of the experiment 4 indicate that the endogenous respiration was an important factor to the overall loss of bacterial viability. This is probably due to the loss of moisture in the biofilm. The comparison between experiments 3 and 4 further demonstrates that spray liquid with nutrient solution could keep the activity of microorganism.

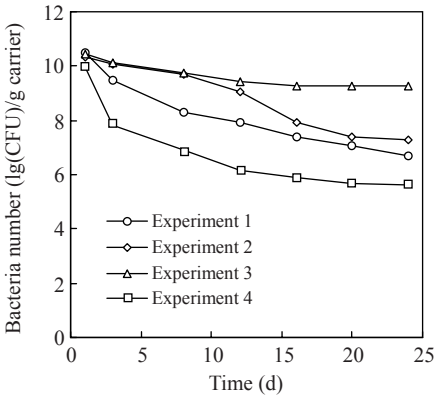

Fig.5 Decrease of live bacteria counts vs starvation time

In contrast to the change of the biomass, the change of live bacteria numbers was more drastic, suggesting that death rate of live bacteria was faster than loss rate of biomass owing to endogenous decay, secondary predation, or oxygen limit. Compared with the biomass, the live bacteria numbers were a more important parameter for resuming high H_2S removal efficiency after the starvation.

Biotrickling filter re-acclimation

Re-acclimation experiments were conducted to investigate the response of these previously acclimated biotrickling filters to starvation periods and evaluate whether the biotrickling filter can recover rapidly and meet the demand of industrial application.

Fig.6 shows the re-acclimation processes of H_2S removal at 6.5 m^3/h of airflow rate and 100 mg/m^3 of inlet H_2S concentration after resuming normal operation. The recovery processes were commenced after a 24-d starvation period. The biotrickling filters could obtain high removal efficiency within 4 d of re-acclimation. Fig.6 provides the results of this recovery process. Re-acclimation after the starvation was much faster than the initial startup phase because of the pre-existence of an acclimated process consortium. The fact that full activity of sulfur-oxidizing bacteria was recovered suggests that re-acclimation did not require the buildup of significant amounts of new degrading biomass.

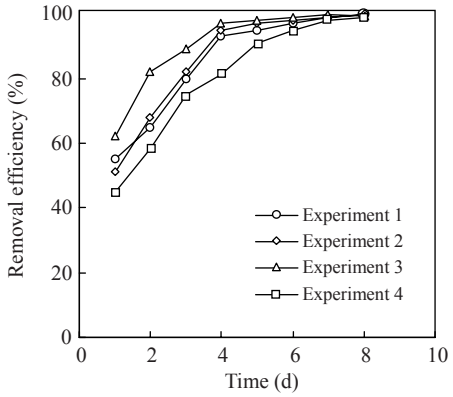

Fig.6 Re-acclimation for H_2S removal after the starvation

Inlet H_2S concentration was kept at a relatively high value at the re-acclimation process without ramping up. This was different from the startup phase of the bioreactor. All the bioreactors could resume high removal efficiency (more than 99%) within 4 d regardless of the operation conditions during the starvation.

Re-acclimation processes of four starvation experiments were similar after restarting biotrickling filters. Re-acclimation of experiment 4 was slower than those of other starvation experiments, which is correlated with the live microorganism numbers in the bioreactors. Compared with other experiments, the live bacteria number was similar at the end of experiments 1 and 2 (16 to 24 d in Fig.5); thus, their re-acclimation periods with complete recovery of the H_2S elimination capacity were nearly uniform after

24 d. Comparison of four different starvation experiments showed that the time for re-acclimation was not obviously affected by the presence or the absence of gas flow or spray liquid. Furthermore, an important implication of these starvation experiments was that significant energy can be saved by shutting the blower and the water pump off during industrial operation, which would not lead to notable adverse effects.

Biotrickling filter response to shock loads

In order to further study the acclimatization of the bioreactor to shock loads, the bioreactor was supplied with H_2S of variable concentration after resuming normal operation. The effect of abrupt changes in H_2S inlet concentration from 2 to 2500 mg/m^3 on the biotrickling filters was investigated under a fixed residence time (τ=41 s). Inlet H_2S concentration of the bioreactor was not allowed to stabilize in the shock loads experiments, which is similar to the practical concentration produced during industrial operation. The momentary response of the bioreactor to these abrupt changes in inlet concentration is presented in Fig.7. Owing to the similarity of the four bioreactors to resist the shock loads, the biotrickling filter after starvation experiment 1 was investigated.

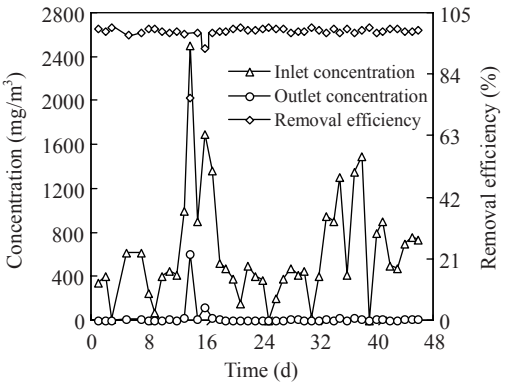

Fig.7 Transient response of biotrickling filter to fluctuating H_2S after re-acclimation

The results show that although H_2S inlet concentration was very unstable ranging from 2 to 1700 mg/m^3, its removal efficiency was stabilized nearly 98%. However at the inlet concentration higher than 1700 mg/m^3, the outlet concentration ascended immediately, and removal efficiency of the bio-trickling filter dropped to lower than 92%. There were two possible reasons for the decrease of removal efficiency at this higher inlet concentration. On the one hand, the experiments were carried out under the high liquid trickling velocity (with 5 L of the nutrient solution, once 1 h) in order to avoid the clogging of the bioreactor, which could limit the increase of biomass and further resulted in the decrease of removal capacity in the bioreactor. On the other hand, a toxic effect of higher concentration of H_2S on the microbial communities could also lead to the decrease of removal efficiency by altering the carrier pH because the bioreactor could produce acidification phenomenon during the long-term operation, as reported in our previous study (Xie *et al*., 2003).

Fig.7 further shows that, when the inlet concentration resumed lower than 1700 mg/m^3, the operation of the bio-trickling filter could rapidly recover to normal state, which indicates that removal efficiency of H_2S could recover to nearly 98% instantly. Therefore, the bioreactor could meet the demand of industrial operation to resist the shock loads.

CONCLUSION

The study suggests that the biotrickling filters were capable of withstanding different conditions of starvation with rapid recovery to high removal efficiency when starvation ceases. Therefore, re-acclimation of the biotrickling filters after starvation was not a major limit factor for H_2S removal. The viable microorganism number was a major indicator for the restart of the bioreactors. In order to keep the activity of microorganism and also save energy, air and nutrient solution could be stopped and only supplied at regular intervals, which could reduce the time for restart. At the same time, starvation was a useful factor to avoid the clogging of the bioreactor, which could reduce the biomass of the bioreactor in a way.

The good removal in dealing with these abrupt changes in inlet H_2S concentration after resuming normal operation suggests that the bioreactor had a strong ability to resist shock loads when it was supplied continuously with H_2S of variable inlet concentration. H_2S pulses to the bioreactor show that, when H_2S concentration was variable, removal efficiency was maintained at high value (more than

98%) except inlet concentration of higher than 1700 mg/m^3. Once the biotrickling filter was supplied with H_2S at inlet concentration of lower than 1700 mg/m^3, its removal efficiency was nearly 98% regardless of previous inlet H_2S concentration. Overall, the results show that the bioreactor could meet the demand of industrial operation to resist the shock loads and starvation condition for H_2S removal.

References

Bandosz, T.J., 2002. On the adsorption/oxidation of hydrogen sulfide on activated carbons at ambient temperatures. *Journal of Colloid and Interface Science*, **246**(1):1-20. [doi:10.1006/jcis.2001.7952]

Bouzaza, A., Laplanche, A., Marsteau, S., 2004. Adsorption oxidation of hydrogen sulfide on activated carbon fibers: effect of the composition and the relative humidity of the gas phase. *Chemosphere*, **54**(4):481-488. [doi:10.1016/j.chemosphere.2003.08.018]

Cox, H.H.J., Deshusses, M.A., 2002. Co-treatment of H_2S and toluene in a biotrickling filter. *Chemical Engineering Journal*, **87**(1):101-110. [doi:10.1016/S1385-8947(01)00222-4]

Hartikainen, T., Martikainen, P.J., Olkkonen, M., Ruuskanen, J., 2002. Peat biofilters in long-term experiments for removing odorous sulphur compounds. *Water, Air and Soil Pollution*, **133**(1-4):335-348. [doi:10.1023/A:1012966705004]

Jiang, X., Yan, R., Tay, J.H., 2009. Transient-state biodegradation behavior of a horizontal biotrickling filter in co-treating gaseous H_2S and NH_3. *Applied Microbiology and Biotechnology*, **81**(5):969-975. [doi:10.1007/s00253-008-1759-9]

Jin, Y.M., Veiga, M.C., Christian, K., 2007. Co-treatment of hydrogen sulfide and methanol in a single-stage biotrickling filter under acidic conditions. *Chemosphere*, **68**(6):1186-1193. [doi:10.1016/j.chemosphere.2007.01.069]

Lee, J.H., Trimm, D.L., Cant, N.W., 1999. The catalytic combustion of methane and hydrogen sulphide. *Catalysis Today*, **47**(1-4):353-357. [doi:10.1016/S0920-5861(98)00317-4]

Le Leuch, L.M., Subrenat, A., Le Cloirec, P., 2003. Hydrogen sulfide adsorption and oxidation onto activated carbon cloths: applications to odorous gaseous emission treatments. *Langmuir*, **19**(26):10869-10877. [doi:10.1021/la035163q]

Liu, Y.H., Xie, Q., Zhao, Y.Z., Chen, S., Zhao, H., 2005. Removal of ternary VOCs in air streams at high loads using a compost-based biofilter. *Biochemical Engineering Journal*, **23**(1):85-95. [doi:10.1016/j.bej.2004.11.002]

Potivichayanon, S., Pokethitiyook, P., Kruatrachue, M., 2006. Hydrogen sulfide removal by a novel fixed-film bioscrubber system. *Process Biochemistry*, **41(**3):708-715. [doi:10.1016/j.procbio.2005.09.006]

Wani, A.H., Branion, R.M.R., Lau, A.K., 1998. Effects of periods of starvation and fluctuating hydrogen sulfide concentration on biofilter dynamics and performance. *Journal of Hazardous Materials*, **60**(3):287-303. [doi:10.1016/S0304-3894(98)00154-X]

Xie, W.M., Zhang, L.H., Wang, Q.H., Chen, H.J., Bo, X., 2003. Treatment of odor containing hydrogen sulfide released in the wastewater of pharmaceutical company by high efficient bioreactor with the packed stuffing. *Environmental Science*, **24**(6):74-78 (in Chinese).