In: Proc. 1998 Conference on Biofiltration, University of Southern California, October 22-23, 1998. F. E. Reynolds Jr. (ed.). The Reynolds Group, Tustin, CA. p. 159-168.

Performance of A Pilot Scale Biotrickling Filter Under Non-Steady State Conditions

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ABSTRACT

The performance of a two-stage pilot/full-scale biotrickling filter was investigated for the treatment of styrene releases from a bathtub manufacturing process. The two-stage system operated in series provided stable performance under highly fluctuating conditions. As a whole, this study illustrates that significant knowledge can be gained from a detailed analysis hourly variation of the reactor performance and from the sensitivity to key operating parameters. The biotrickling filter was moderately susceptible to 2 days of starvation during weekend recess. When styrene and toluene were fed alternatively at 3-hour intervals, effective toluene removal was rapidly observed although the reactor had never been exposed to toluene prior to the experiment. Toluene elimination increased over time as a result of adaptation of the process culture to the new pollutant. The experimental results showed that biotrickling filtration is a promising control technology for the treatment of contaminated air streams subject to fluctuations both in concentration and in composition.

INTRODUCTION

Biofilters and bioscrubbers are the most common bioreactors for air pollution control. Problems associated with biofilters include difficulties in controlling pH and nutrients in the packing materials. In the case where halogenated or sulfur-containing compounds are treated, acidic metabolites are produced, which exhausts the buffering capacity and reduces the pH in the packing materials. The biotrickling filter has advantages for dealing with some of these problems. Because of the water recirculation in biotrickling filters, acidic byproducts and excess biomass can be drained, and optimum pH and nutrients can be maintained over time. Methylene chloride (Diks and Ottengraf, 1991; Hartmans and Tramper, 1991; Zuber, 1995), hydrogen sulfide (Morton and Caballero, 1997), chlorinated benzene (Mpanias and Baltzis, 1998), and ammonia (Smits et al., 1995) produce acidic metabolites and have been successfully treated in biotrickling filters. Other biotrickling filter research showed that benzene, toluene, styrene, and other volatile organics could be effectively removed in laboratory-scale biotrickling filters. (Togna and Singh, 1994; Holubar et al., 1995; Schindler and Friedl, 1996; Fortin and Deshusses, 1997; Pedersen et al., 1997; Cox et al., 1998)

While many field applications of biofilters have been reported, limited data exist for the similar field operation of biotrickling filters (Loy et al., 1997; Webster et al, 1998). Most previous biotrickling filter studies were conducted at laboratory scale under

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steady state conditions. However, biotrickling filters often exhibit different performance when applied in the field because of varying operating conditions.

This paper presents the field performance of a pilot/full-scale biotrickling filter treating styrene releases from a bathtub manufacturing process. The purpose of this study was to investigate the responses of the biotrickling filter under varying environmental conditions. Effect of hourly concentration variation, system starvation, and cyclic change of feed compounds (styrene and toluene) on the biotrickling filter performance were investigated.

METHODS AND ANALYSIS

Methods

A two-stage biotrickling filter was designed based on the previous bench-scale laboratory experiments (Zuber et al., 1997). Each reactor had an internal diameter of 1.6 m, height of 2.4 m, and bed volume of 4.1 m^3 (Figure 1). The packing material consisted of 9 cm Jaeger tri-pack spheres with a 95 % void space and a surface area of 125 m^2 m^{-3}. The biotrickling filter was operated in series with an average gas flow rate of 357 m^3 h^{-1} (210 scfm) and empty bed residence times of 42 seconds per reactor. Contaminated gas and recycled liquid were fed co-currently to the top of the biotrickling filter. A volume of 0.8 m^3 of water was maintained in the base of each tank. Liquid was recycled with average flow rates of 13.8 m^3 h^{-1} for each reactor. During normal operation, an average of 20 L h^{-1} of recycle liquid was replaced by fresh mineral medium solution containing 0.7g L^{-1} of N, 1.2 g L^{-1} of P, 0.8 g L^{-1} of K, and trace elements. The fresh liquid served for drainage of potential metabolite and excess biomass, and makeup for losses from evaporation. The pH of recirculated water ranged from 6.1 to 7.2 and averaged 6.8. The pH of recirculated water was maintained using a 5 % NaOH solution. The reactor setup included a programmable logic controller (PLC) unit with Labview Software (National Instruments, Austin, TX) to monitor and control the system. Further details of reactor design, operation, and cost analysis are discussed elsewhere (Webster et al., 1998; Deshusses and Webster, 1998).

After 7 months operation treating styrene exhaust from manufacturing process, an experimental protocol was developed to study the effect of stepwise input of toluene and styrene on performance. For these studies, the biotrickling filter was disconnected from the plant stack, and synthetic waste air was produced by pumping either styrene or toluene directly into the inlet air. Each cycle consisted of an average of 0.69 g m^{-3} of styrene treated for 3 hours, a 1-hour resting period with no volatile organic carbons, a 3-hour period where an average concentration of 0.58 g m^{-3} of toluene was treated, and a final 1-hour resting period. Each complete cycle took 8 hours of operation, and 16 cycles were completed in a row.

Figure 1. The pilot/full-scale biotrickling filter.

Analysis

Total gas phase contaminant concentrations were measured with a flame ionization detector (FID; SRI Instruments, Torrance, CA). The air sampling system collected air samples from air sampling lines before reactor 1, between reactors (outlet 1), after reactor 2 (outlet 2), and from ambient air for three minutes in each sampling location. After the completion of each cycle, the system back flushed the sampling lines for three minutes, and started the cycle again. 15 minutes were needed to complete the sequence.

RESULTS AND DISCUSSION

Hourly Variation of Biotrickling Filter Performance

The concentration of styrene in the off-gases from the bathtub manufacturing process fluctuated cyclically during normal operation. The inlet concentrations in a specific day varied from 0.03 g m^{-3} to 0.83 g m^{-3} (Figure 2). While average and standard deviation of inlet, between tank (outlet 1), and final (outlet 2) concentrations were 0.58 $\pm$ 0.22 g m^{-3}, 0.27 $\pm$ 0.11 g m^{-3}, and 0.10 $\pm$ 0.04 g m^{-3}, their median concentrations were 0.66 g m^{-3}, 0.31 g m^{-3}, and 0.10 g m^{-3}, respectively. The pattern of normal probability plot for inlet and outlet concentrations at the same day showed that outlet 2 concentrations were relatively stable compare to highly varying inlet concentrations (Figure 3). The sigmoid distribution of the inlet concentration reflects the intermittent emission pattern. While the biotrickling filter received virtually no pollutants 10% of the time, concentrations usually ranged from 0.6 to 0.8 g m^{-3} when emissions occurred (about 80% of the time). As a rule, such inlet and, if possible, outlet distribution plots should be part of the problem definition during biotrickling filter evaluation. They should be made during typical plant operation and will enable to size the bioreactor for the most probable emissions, adding pretreatment or post-treatment, if intermittent operation is found to induce short, but unacceptable emission breakthrough.

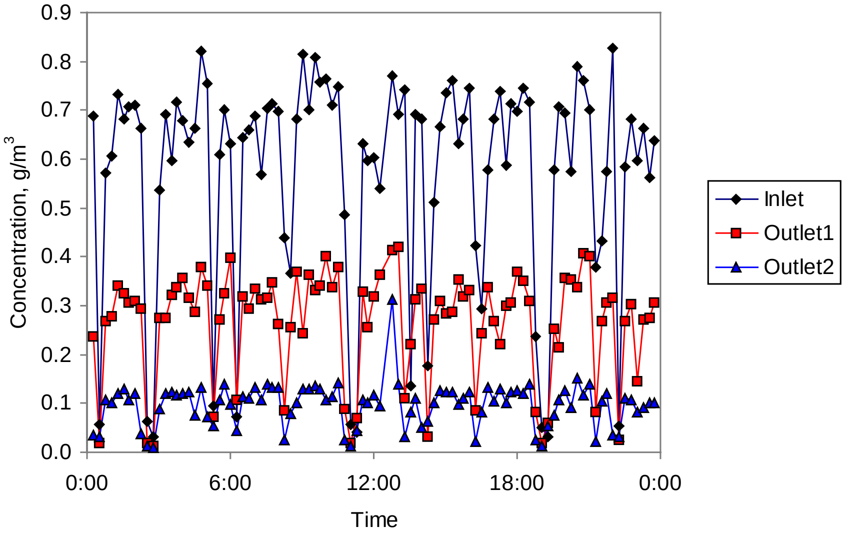

Figure 2. Hourly variations of styrene concentration in a biotrickling filter on a specific day (July 30, 1997).

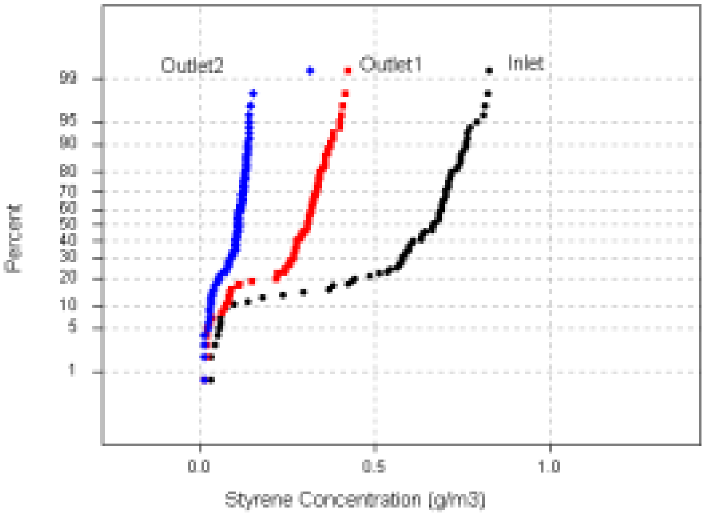

Figure 3. A normal probability plot of styrene concentrations in a specific day (July 30, 1997).

The relationships between loading rate (L) and elimination capacity (EC) for the overall biotrickling filter, for stages 1 and 2 are shown in Figure 4. Performance of stage 1 showed two linear distributions (Figure 4, middle). This peculiarity is due to the sudden increase or decrease of inlet concentration and combined with delayed sampling for concentration measurements. A single linear relationship between L and EC was found in stage 2 and for the entire biotrickling filter showing a first order kinetic and high removal percentages at loadings up to 35 g $m^{-3} \cdot h^{-1}$. Overall, the two-stage setup provided stable performance under fluctuating inlet concentration.

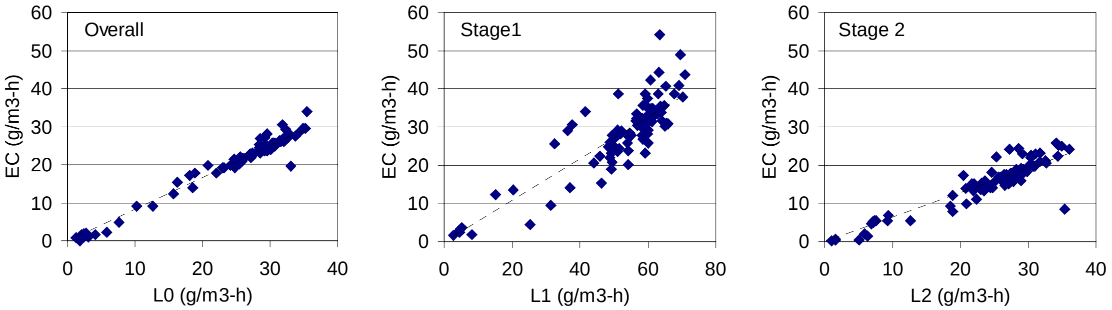

Figure 4. Correlation among loading rates L (g m$^{-3}\cdot$h^{-1}) and elimination capacities EC (g m$^{-3}\cdot$h^{-1}) on a specific date (July 30, 1997). The numbers 0, 1, and 2 denote overall, stage 1, and stage 2, respectively. The values for overall inlet loading (L_0) were half of the first stage inlet loading (L_1) because the system was operated with the two reactors in series.

Over several months of operation, the elimination capacity for the first tank remained relatively constant (ca. 27 g m$^{-3}\cdot$h^{-1}) at loading rates higher than 50 g m$^{-3}\cdot$h^{-1} while the performance of the second tank followed the loading rate. This performance was similar to those of Loy and Flauger (1996). They reported the first-order reaction kinetic for loadings of less than 30 g m$^{-3}\cdot$h^{-1}, and zero-order kinetics with loading rates greater than 40 g m$^{-3}\cdot$h^{-1} and virtually 100% removal at loading rate lower than 25 g m$^{-3}\cdot$h^{-1} (Loy et al., 1997). In our case, when styrene was added to the system either with or without manufacturing styrene discharges to extend the range of daily loading rates to about 60 g m$^{-3}\cdot$h^{-1} (120 g m$^{-3}\cdot$h^{-1} across tank 1), the elimination capacity occasionally reached 65 g m$^{-3}\cdot$h^{-1} in tank 1. This is a high value for styrene. Still, our field performance was lower than bench-scale laboratory data reported in literature (Togna and Singh, 1994; Loy et al., 1997; Chou and Hsiao, 1998). More than 90% removal efficiency was reported for styrene at loads up to 300 g m$^{-3}\cdot$h^{-1} and an empty bed residence time of 0.5 minutes in a laboratory biotrickling filter (Togna and Singh, 1994). But the high performance could not be followed by similar field achievements. In our case, several factors may have caused lower performance in the field. Because of the nature of manufacturing process, the system was not provided with substrate about 10-15% of the day, and during the weekend recess. The biological activity was not optimum under non-steady environmental conditions. In contrast, our system did not experienced clogging problems, a sign that the process culture was subject to a significant stress. This together with occasional system malfunctions and other biological limitations probably affected pollutant elimination (Webster et al., 1998). Mass transfer limitation might be another factor. The gas superficial velocity (137 m h^{-1}) and the high Henry's law coefficient of styrene (H=0.15) may also have limited styrene mass transfer on the biofilm. When the air flow rate was reduced by 50%, the removal efficiency reached more than 90 % (Deshusses and Webster, 1997). Clearly, further detailed studies are warranted to determine the true contribution of each limiting factor in the overall reaction kinetic.

Effect of Weekend Starvation

After that the system was found not to be seriously affected by a few hours of down time, the effect of 2 days starvation on treatment performance was examined in detail. While air blower and water pumps were operated, no substrate was fed to the biotrickling filter (system starvation during the weekend recess). Cumulative removal and elimination capacity were defined (Equations 1-3) to assess the impact of starvation.

$$CEC = (M_0 – M_2)(V)^{-1}(t_s)^{-1} \qquad (1)$$
$$CRE = 100(1- M_2/M_0) \qquad (2)$$
$$Mi = \Sigma\, Q(C_{i,i} + C_{i,j-1})(\, t_i + t_{i,j-1})/2 \qquad (3)$$

where, CEC = cumulative elimination capacity ($g\ m^{-3}\cdot h^{-1}$),
CRE = cumulative removal efficiency (%),
M_0 and M_2= cumulative mass in inlet and outlet, respectively (g),
Q = air flow rate ($m^3\ h^{-3}$),
Cij = styrene concentration at time j for sample i ($g\ m^{-3}$),
i= 0 for inlet and 2 for tank 2 outlet,
V = bed volume (m^3), and
t_s = elapsed time (h).

The cumulative mass removal efficiency, CRE initially decreased for 30 minutes, and increased up to 70% between 12 to 17 hours after system restart (Figure 5). The cumulative elimination capacity did not exhibited a similar maximum but it also reached a quasi steady-state within 36-40 hours. Other experiments (not shown) demonstrated that the recovery after a 3-day starvation was much slower.

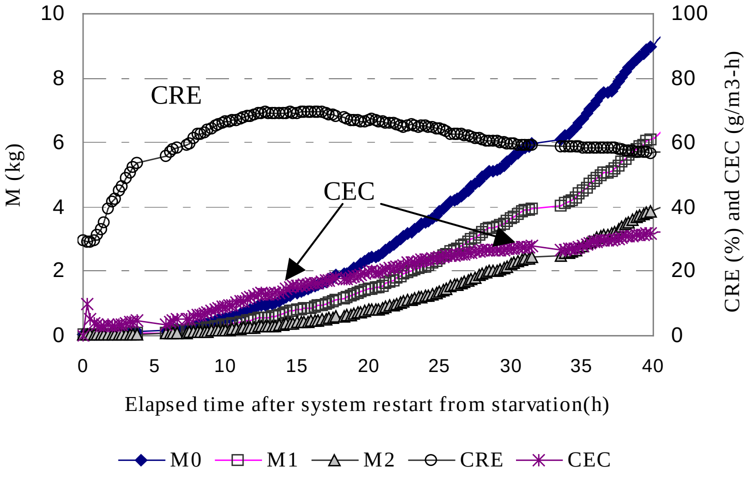

Figure 5. Cumulative styrene masses in inlet (M0) outlet 1 (M1), and outlet 2 (M2), and efficiencies (CRE) and overall elimination capacities (CEC) after restarting from 2 days starvation.

As discussed by Jenkins and Heald (1996), total loss of toluene-induced protein occurred in after 300 to 600 hours of starvation in suspended cultures. This was much longer than the starvation experienced by the biotrickling filter for styrene. However, Jenkins and Heald (1996) found that the ability of the culture to degrade toluene fell much more sharply with approximately 75 % of the activity lost within the first 50 hours. This may explain the much slower recovery of the biotrickling filter after more than 2 days of starvation. From a pollutant emission standpoint, the asymptotic behavior of the cumulative removal and cumulative elimination capacity, shown in Figure 5 suggests that the effects of starvation are minimal if the frequency of severe starvation is less than one event in 48 hours. Still, the long-term effects of repeated starvation at a high frequency on the process culture remain to be quantified.

Effect of Alternating Substrate Input

The effect of cyclically alternating inputs of styrene and toluene on biotrickling filter performance was investigated using a synthetic air stream. Each cycle consisted of 3-hour toluene supply, 1-hour rest, 3-hour styrene supply, and 1-hour rest. 16 consecutive cycles were completed. The biotrickling filter had been only exposed to styrene prior to the experiment. The patterns for styrene and toluene removal were quite different. Styrene removal efficiency was quite consistent, remaining essentially constant over the period of the experiment, and showing little change within each cycle. In contrast, toluene removal efficiency increased as the number of cycles increased, and also increased rapidly within each cycle. The inlet, outlet 1 and outlet 2 concentrations for selected cycles (1, 5, and 13) are reported in Figure 6. During the first cycle, inlet concentrations fluctuated slightly as a result of adjustments made in the pumping rate to achieve the target inlet concentration of approximately 0.6 g m^{-3}. Detailed examination of the data at the time of the step changes (up or down) shows that sorption was minimal and acclimation rapid especially for styrene. Transient behavior lasted less than one hour for styrene. Toluene treatment improved more slowly, but eventually reached pseudo steady state during the 3-hour step inputs. Comparison of cycles 1,5, and 13 (Figure 6) shows that styrene concentration patterns were very similar over the cycles. This was expected because the reactor had been exposed to styrene for the past 7 months and those short periods of starvation did not damage the process culture as discussed in the previous section. On the other hand, toluene concentration patterns showed that a significant improvement occurred over the cycles. Careful data analysis revealed that the improvement over time was not so much in the ultimate value for the elimination capacity (about 10-12 g $m^{-3}\cdot h^{-1}$) but more in the time needed to reach a (pseudo) steady state. This decreased from about 3 hours to less than 1.5 hours in less than 5 cycles. Indeed, the elimination capacities of the first and second stages were not significantly different, although loadings were different because the reactors were connected in series. Presumably elimination kinetics had reached a zero-order regime and were no longer a function of the loading.

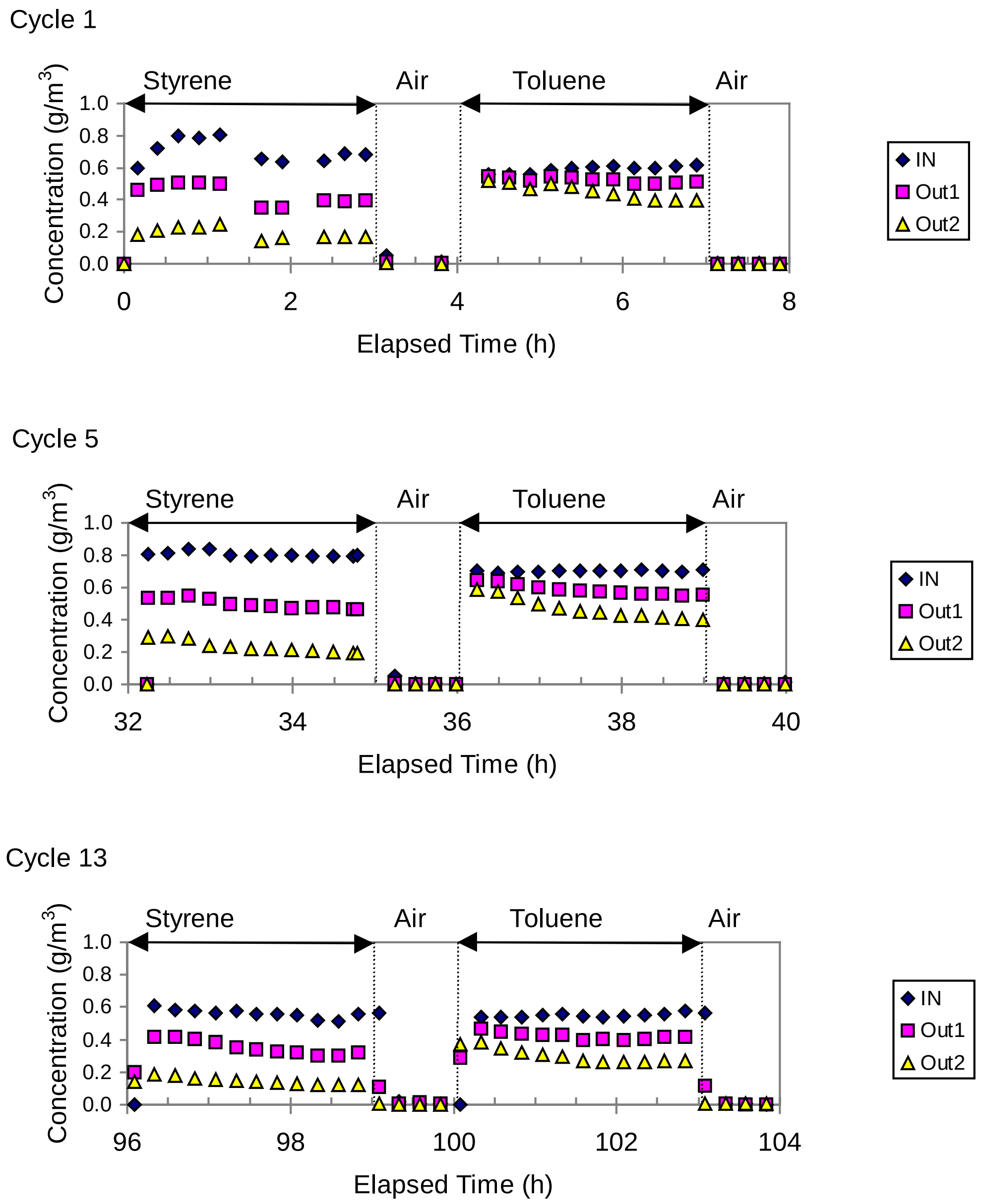

Figure 6. Effect of alternating inputs of styrene and toluene on the concentration changes at different cycles.

CONCLUSIONS

The field operation of a pilot/full-scale biotrickling filter for the treatment air contaminated with styrene from a bathtub manufacturing facility was analyzed in detail. It revealed that the fluctuating styrene loading and the low concentrations received by the biotrickling filter affected its performance. Even so, styrene was fairly well removed. The average elimination capacity was 10 to 30 g m^{-3} h^{-1} with 55-85% removal at relatively low loadings (20-40 g m^{-3} h^{-1}). This performance could be sustained over several months, which was often not the case in previous styrene degrading biofilter and biotrickling filter studies. During the field study, the low loading may have precluded to higher performance since the reactors were shown to be mostly limited by the biological reaction.

Since the reactors were affected by fluctuating conditions, two experiments were designed. In the first one, the effect of starvation was investigated in greater details. The use of cumulative removal and cumulative elimination capacity allowed to determine both the short term and long term impact of starvation. It revealed that if the starvation was shorter than 48h, the effect of starvation would become negligible both on the instantaneous and on the cumulative pollutant removal after less than 20h. In the second experiment, styrene and toluene were alternately fed to the biotrickling filter. While the reactor had never been exposed to toluene prior to the experiment, effective toluene removal was rapidly observed. Toluene elimination increased over the number of cycles due to the adaptation of the process culture to the new pollutant. This rapid adaptation took from 16 to 40 hours and proves that biotrickling filters can be used for the treatment of highly changing air streams.

Overall, the results presented herein stress that detailed analysis of bioreactor parameters is a key to understanding the effects of process variables. While this is too often overlooked, there is no doubt that gaining insight into the biotrickling filter process is the key to better reactor designs, improved reactor operation and better process controls.

REFERENCES

Chou, M.-S. and C.-C. Hsiao (1998), “Treatment of styrene-contaminated air stream in biotrickling filter packed with slags”, *J. Environ. Eng.*, **124**(9): 844-850.

Cox, H. H. J., T. T. Nguyen, and M. A. Deshusses (1998), “Elimination of toluene vapors in biotrickling filters: Performance and carbon balances", In: Proceedings of the 91st Annual Meeting and Exhibition of the Air & Waste Management Association, Air and Waste Management Association, Pittsburgh, PA.

Deshusses, M.A. and T.S. Webster (1998). "Construction and economics of a pilot/full-scale biological trickling filter reactor for the removal of VOCs from polluted air", *J. Air Waste Manage. Assoc.* (submitted).

Diks, R. M. M. and S. P. P. Ottengraf (1991), “Verification studies of a simplified model for the removal of dichloromethane from waste gases using a biological trickling filter (Part II)”, *Bioprocess Engineering*, **6**(3): 131-140.

Fortin , N. Y., and M. A. Deshusses (1998), “Treatment of MTBE vapors in biotrickling filters: 1. Reactor startup, steady-state performance, and culture characteristics”, *Environ. Sci. Technol*. (submitted)

Hartmans, S. and Tramper J. (1991), “Dichloromethane removal from waste gases with a trickle-bed bioreactor”, *Bioprocess Engineering*, **6**: 83-92.

Holubar, P., Andorfer C., and R. Braun (1995), “Prevention of clogging in trickling filters for purification of hydrocarbon-contaminated air” In: Proceedings of the 1995

Conference on the Biofiltration, 199-206, Hodge, D. and Reynolds, F. E. Jr. (Eds.), Los -Angeles, CA, October.

Jenkins, R. O., and S. C. Heald (1996), "Stability of toluene oxidation by *Pseudomonas putida* under nutrient deprivation", *Appl. Microbiol. Biotechnol.*, **46**(4):388-392.

Loy J, K and M. Flauger (1996), "Biological elimination of styrene contaminated waste gas with the Zander biotrickling technology" In: Proceedings of the 89th Annual Meeting and Exhibition of the Air & Waste Management Association. Air & Waste Management Association, Pittsburgh, PA

Loy J, K. Heinrich, and B. Egerer (1997), "Influence of filter material on the elimination rate in a biotrickling filter bed", In: Proceedings of the 90th Annual Meeting and Exhibition of the Air & Waste Management Association. Air & Waste Management Association, Pittsburgh, PA

Morton, R. L. and Caballero R. C. (1997), "Removing hydrogen sulfide from wastewater treatment facilities", In: Proceedings of the 90th Annual Meeting and Exhibition of the Air & Waste Management Association, Air and Waste Management Association, Pittsburgh, PA.

Mpanias, C. J. and B. C. Baltzis (1998), "An experimental and modeling study on the removal of mono-chlorobenzene vapor in biotrickling filters", *Biotech. Bioeng.*, **59**(3): pp. 328-343.

Pedersen, A. R., S. Moller, S. Molin, and E. Arvin (1997), "Activity of toluene-degrading *Pseudomonas putita* in the early growth phase of a biofilm for waste gas treatment", *Biotech. Bioeng.*, **54**(2): 131-141.

Smits, M. C. J., S. P. P. Ottengraf, and J. C. van den Heuvel, "Effect of the superficial velocity on the nitrification of ammonia polluted air in a bio-trickling filter", In: Proceedings of the 1995 Conference on the Biofiltration, 199-206, Hodge, D. and Reynolds, F. E. Jr. (Eds.), Los Angeles, CA, October.

Schindler, I and A. Friedl (1996), “Optimization of trickle-bed reactors for waste gas cleaning using a toluene contaminated gas stream”, In: Proceedings of the 1996 Conference on the Biofiltration, 198-205, Hodge, D. and Reynolds, F. E. Jr. (Eds.), Los Angeles, CA, October.

Togna, A. P. and M. Singh (1994), “Biological vapor-phase treatment using biofilter and biotrickling filter reactors: Practical operating regimes”, *Environ. Prog.*, **13** (2): 94-97.

Webster, T. S., H. H. J. Cox, and M. A. Deshusses (1998), "Resolving performance problems encountered in the use of a pilot/full-scale biotrickling filter reactor", *Environ. Prog.*, (submitted).

Zuber, L.(1995), Trickling filter and three-phase airlift bioreactor for the removal of dichloromethane from air, Ph.D. Thesis, Swiss Federal Institute of Technology, Zurich, Switzerland.

Zuber, Laurent, Irving J. Dunn, and Marc A. Deshusses (1997), Comparative scale-up and cost estimation of a biological trickling filter and a three-phase air lift bioreactor for the removal of methylene chloride from polluted Air", *J. Air Waste Manage. Assoc.*, **47**: 969-975.