Appl Microbiol Biotechnol (2000) 54: 133–137

ORIGINAL PAPER

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Toluene degradation in the recycle liquid of biotrickling filters for air pollution control

Received: 16 June 1999 / Received revision: 17 November 1999 / Accepted: 15 December 1999

Abstract Pollutant degradation in biotrickling filters for waste air treatment is generally thought to occur only in the biofilm. In two experiments with toluene degrading biotrickling filters, we show that suspended microorganisms in the recycle liquid may substantially contribute to the overall pollutant removal. Two days after reactor start up, the overall toluene elimination capacity reached a maximum of 125 g m^{-3} h^{-1}, which was twice that found during prolonged operation. High biodegradation activity in the recycle liquid fully accounted for this short-term peak of pollutant elimination. During steady-state operation, the toluene degradation in the recycle liquid was 21% of the overall elimination capacity, although the amount of suspended biomass was only 1% of the amount of immobilized biomass. The results suggest that biotrickling filter performance may be improved by selecting operating conditions allowing for the development of an actively growing suspended culture.

Introduction

Biological treatment is an emerging technology for air pollution control. Two reactor types show the most promise as alternatives to physical and chemical treatments: biofilters and biotrickling filters. Biofilters have been used successfully for odor abatement and to a lesser extent for volatile organic compound control in industry for several decades (Devinny et al. 1999). Waste air treatment in biotrickling filters is a newer but promising technique allowing higher pollutant elimination capacities to be obtained for a broader range of pollutants (Cox and Deshusses 1998).

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In biotrickling filters, polluted air is passed together with a recycle liquid through a packed bed on which a pollutant-degrading biofilm develops. One assumption commonly made for biotrickling filter modeling purposes is that biodegradation takes place only in the biofilm, i.e., that the liquid phase only mediates mass transfer of pollutants into the biofilm, and biodegradation by suspended cells is ignored. However, we regularly observed high concentrations of suspended biomass in the recycle liquid of toluene-degrading biotrickling filters which correlated with a high pollutant elimination. In the present paper, we demonstrate that biodegradation in the recycle liquid significantly contributes to the overall elimination capacity. Factors affecting pollutant degradation in the liquid phase are identified and discussed.

Materials and methods

Experimental set-up and standard operation of biotrickling filters

The performance during reactor start-up was determined using periodically rotating biotrickling filters which have been described elsewhere (Cox and Deshusses 2000). Biotrickling filters consisting of a packed bed (height 0.5 m, diameter 0.04 m) and two identical liquid reservoirs attached to both sides of the bed were periodically rotated. In the resting position, 0.35 l (0.3 l in some experiments) of liquid in the upper reservoir were trickled down through the reactor and were collected in the lower reservoir. The biotrickling filters were then rotated through 180°, i.e., changing the position of the liquid reservoirs, to reinitiate the trickling process. During the experiments the rotation frequency was every 111 s, which resulted in an average liquid superficial velocity of 9.0 m h^{-1}.

The rotating reactors contained a packing of crushed PP Pall rings (irregular size, 0.5–2 cm, Koch Engineering, Wichita, Kan.) with a specific surface area of approximately 450 m^2 m^{-3}. On day 0, 0.35 l of a mineral medium (Cox and Deshusses 1999) and 10 ml of a seed culture from the conventional biotrickling filter described below were added to each reactor and standard operation was initiated. Toluene contaminated air (20–25 °C, toluene concentration of 1.8–2.2 g m^{-3}) was supplied at an average gas flow rate of 0.05 m^3 h^{-1} (volumetric load of 80 m^3 m^{-3} h^{-1}). On a daily basis, 0.15 l of the liquid phase was withdrawn and replaced by fresh mineral medium. Deionized water was added to compensate for evaporative losses. Under standard operating conditions, it was

shown that the rotating biotrickling filters behaved similarly to conventional biotrickling filters (Cox and Deshusses 2000).

Steady-state performance was investigated using a conventional biotrickling filter with a packed bed volume of 23.6 l (height 1.3 m, diameter 0.152 m) containing 2.56 cm PP Pall rings (specific surface area 220 m^2 m^{-3}; Koch Engineering). At the time of the investigation, the biotrickling filter had been treating toluene for over 1 year. Liquid and air flow (22–24 °C) were cocurrent from top to bottom at rates of 140 l h^{-1} and 1.5 m^3 h^{-1}, respectively. The recycle liquid (3 l total) was recycled using a centrifugal pump. Fresh mineral medium was continuously supplied at a rate of 0.25 l h^{-1}. Toluene inlet concentrations in the inlet air was 0, 1, or 2 g m^{-3} depending on the experiment.

Specific experiments

The contribution of the degradation in the liquid phase to the overall toluene elimination capacity (EC) during start-up was investigated using two identical rotating biotrickling filters. Toluene inlet and outlet concentrations were determined using a flame ionization detector at regular intervals over a period of 8 days after inoculation. Toluene degradation in the recycle liquid was assessed by taking liquid samples, followed by immediate analysis in a biological oxygen uptake rate (OUR) meter.

The contribution of the degradation in the liquid phase to the overall EC during steady-state operation was determined using conventional biotrickling filters. The experiment was based on the assumption that reducing the suspended biomass concentration in the recycle liquid would result in a prorated lower overall EC. For this, the EC of the biotrickling filter was determined by analyzing the outlet air before and after replacing the culture liquid with the same volume (3 l) of deionized water. The toluene inlet concentration (2 g m^{-3}), gas flow rate (1.5 m^3 h^{-1}), and all other operating conditions were kept constant to allow direct comparison, except that the fresh medium supply was stopped after changing to the recycling of deionized water. The duration of the experiment was 6.5 h, and the inlet and outlet air and the recycle liquid were regularly sampled for analysis of toluene and total carbon, respectively. As a measure of the biological activity of the liquid during recycling of the culture liquid and the deionized water, respectively, the OUR was determined.

The influence of toluene loading and nutrient supply on the suspended biomass concentration in the recycle liquid was determined as part of previous research on the carbon balance of toluene-degrading biotrickling filters (Cox et al. 1998). Over a period of 7 months, steady-state performance of conventional biotrickling filters was determined at toluene inlet concentrations of 0, 1, or 2 g m^{-3} and while continuously supplying either mineral medium or a phosphate buffer (1 g l^{-1} KH_2PO_4, 1 g l^{-1} K_2HPO_4, pH 6.6). All other operating conditions were as described above. During the experiments, the biotrickling filter contained between 6 and 12 kg biomass. Steady-state total carbon in the recycle liquid was determined as a measure of suspended biomass when the biotrickling filter showed constant toluene degradation and CO_2 production, generally 5–10 days after the operating conditions were changed.

Analytical methods

Toluene gas phase concentrations were determined either by gas chromatography (Cox and Deshusses 1999) or by direct injection of gaseous grab samples into a flame ionization detector (SRI; Las Vegas, Nev.). Toluene ECs were calculated from at least three determinations of both the inlet and outlet air. The amount of wet immobilized biomass on the packing was determined by subtraction of the weight of the clean and dry reactor from the weight of the reactor after draining the liquid for 10 min. Carbon biomass was calculated using conversion factors of 0.046 g dry biomass g^{-1} wet biomass and 0.44 g carbon g^{-1} dry biomass (Cox and Deshusses 1999). Total carbon in the recycle liquid was determined using a Shimadzu (Kyoto, Japan) Total Carbon Analyzer. Concentrations of inorganic and dissolved carbon were a minor fraction of total carbon, hence total carbon in the liquid was considered to be a measure of suspended biomass. OURs were determined using a YSI oxygen monitor (Yellow Springs, Ohio). Samples from the recycle liquid were placed in a 2.7-ml glass chamber, aerated to reach oxygen saturation, and closed for monitoring of the endogenous OUR (usually between 100% and 80% dissolved oxygen). Toluene was then injected (0.19 mM) and OUR was monitored. The toluene-induced OUR was obtained by subtracting the endogenous OUR. All samples were analyzed immediately after sampling and the duration of the analysis did not exceed 20–30 min. OURs were converted to toluene degradation rates using a molar oxygen to toluene ratio of 4.4. This value was experimentally determined by adding limiting amounts of toluene (2–20 μM) to typical samples of the recycle liquid and measuring the oxygen required to deplete the added toluene.

Results

Toluene degradation in the recycle liquid during start-up

The overall toluene EC and the biological activity of the recycle liquid measured by OUR during start-up are shown in Fig. 1. By using a seed culture already adapted to toluene degradation in biotrickling filters, a rapid start-up was observed and the overall toluene EC reached a maximum of 125 g m^{-3} h^{-1} only 47 h after inoculation. Thereafter, the overall EC stabilized at a value of 60 g m^{-3} h^{-1}.

The peak of performance was accompanied by a high toluene-induced OUR in the recycle liquid (Fig. 1). The highest rate observed was 5.7 mg O_2 l^{-1} min^{-1} after 47 h operation, at which time formation of a yellow color, presumably a toluene metabolite (Bertoni et al. 1996), was observed in the recycle liquid. Prolonged operation resulted in disappearance of the yellow color, and biological activity in the recycle liquid decreased to a much lower level. The apparent correlation (inset Fig. 1) between the overall EC and biological activity in the recycle liquid suggests that toluene degradation by suspended biomass significantly contributed to the overall

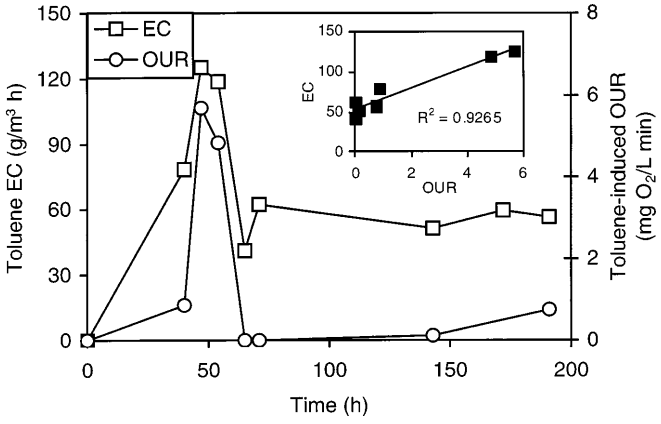

Fig. 1 Average overall toluene elimination capacity (EC) and toluene-induced oxygen uptake rate (OUR) in the recycle liquid of duplicate rotating biotrickling filters during start-up. *Inset* shows the correlation between EC and OUR

EC during early start-up. The toluene-induced OUR observed corresponds to a toluene degradation rate in the recycle liquid of 107 g m^{-3} h^{-1} (expressed per volume of packed bed; note that the liquid volume was 0.3 l). It is interesting to compare this value of 107 g m^{-3} h^{-1} to the difference between the maximum EC 2 days after inoculation (125 g m^{-3} h^{-1}) and the steady-state EC during prolonged operation (60 g m^{-3} h^{-1}), which amounts to 65 g m^{-3} h^{-1}. The latter number is the extra pollutant elimination observed during start-up, presumably due to suspended biomass. It compares reasonably well with the degradation in the liquid determined by OUR (107 g m^{-3} h^{-1}).

Toluene degradation in the recycle liquid during steady-state operation

A direct approach to quantifying the extent of toluene degradation in the recycle liquid is to determine the overall EC of the biotrickling filter before and after removing suspended biomass from the recycle liquid. This was done with the conventional biotrickling filter when the turbidity in the recycle liquid phase was high.

As shown in Fig. 2, replacement of the culture liquid with the same volume of deionized water resulted in a decrease of total carbon from 762 to 162 mg l^{-1}. At the same time, the gas phase toluene outlet concentration significantly increased. The 1-h delay before a new steady state was reached was presumably due to transient absorption of gaseous toluene into water. The steady toluene outlet concentration was 1.41 g m^{-3}, compared to 1.26 g m^{-3} when recycling the liquid culture.

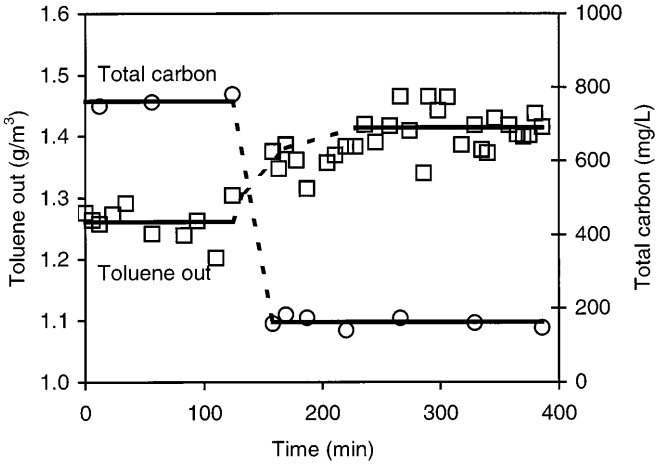

Fig. 2 Effect of replacing of the culture recycle liquid (before 124 min) with water (after 158 min) in a conventional biotrickling filter on the toluene gas outlet concentration (□) and total carbon (○) in the recycle liquid; *solid lines* show the average value for each phase

A summary of the experiment is presented in Table 1. Although replacement of the culture liquid with water caused only a 79% reduction of suspended total carbon, OUR experiments showed that the toluene oxidation activity in the recycle liquid decreased to almost zero. Hence, the higher overall EC while recycling the culture liquid as compared to the overall EC while recycling

Table 1 Overview of steady-state performance of a 23.6 l toluene-degrading biotrickling filter while recycling the culture liquid or while recycling the same volume of deionized water. *EC* Elimination capacity, *OUR* oxygen uptake rate

	Recycle culture liquid	Recycle water
Operating parameters		
Toluene inlet gas concentration (g m^{-3})	2.0	2.0
Volumetric gas load (m^3 m^{-3} h^{-1})	64	64
Liquid volume (l)	3	3
Superficial liquid velocity (m h^{-1})	7.9	7.9
Measured parameters		
Toluene outlet gas concentration (g m^{-3})	1.261	1.414
Total carbon in liquid (mg l^{-1})	762	162
Toluene-induced OUR in liquid (mg O_2 l^{-1} min^{-1})	2.88	0.13
Wet immobilized biomass (kg)	9.04	9.04
Elimination capacities (per volume of packed bed)		
Overall elimination capacity (g m^{-3} h^{-1})	47.0	37.3
Toluene EC in liquid (g m^{-3} h^{-1})		
– calculated from OUR experiments	14.4	0.6
– by difference $EC_{with\ culture} - EC_{with\ water}$	9.7	N/A
Toluene EC in biofilm[a] (g m^{-3} h^{-1})	37.3	37.3
Total carbon distribution		
Suspended total carbon (g)	2.3	0.5
Immobilized total carbon (g)	183	183
Specific biodegradation activities[b]		
– of suspended biomass (mg toluene g^{-1} carbon h^{-1})	99.5[c]	0
– of immobilized biomass (mg toluene g^{-1} carbon h^{-1})	4.8	4.8

[a] By difference of overall EC–toluene EC in liquid
[b] Toluene degradation rates in liquid or in biofilm divided by total amount of suspended and immobilized total carbon, respectively
[c] Value of 148 mg g^{-1} h^{-1} is obtained if the degradation rate of 14.4 g m^{-3} h^{-1} is taken instead of 9.7

water was entirely due to toluene degradation by suspended biomass. With this approach it is assumed that the toluene degradation rate in the biofilm remains the same while changing to the recycle of deionized water. Independent experiments (not shown) confirmed that sudden exposure to deionized water did not cause a shock to the process culture. The overall toluene EC decreased from 47.0 to 37.3 g m^{-3} h^{-1} after the culture liquid was replaced with deionized water (Table 1). Therefore the rate of toluene degradation by suspended biomass in the biotrickling filter was estimated by difference to be 9.7 g m^{-3} h^{-1}, or 22% of the overall toluene EC.

At the time of the experiment, the reactor contained 9.04 kg wet immobilized biomass, while total carbon determinations of the recycle liquid revealed that the amount of suspended biomass was about 1.3% of that value (Table 1). This suggests that the average specific activity of suspended biomass in the biotrickling filter was about 20 times higher than the average activity of the immobilized biomass when expressed per amount of total carbon (Table 1).

Influence of operating conditions on biomass concentrations in the recycle liquid

Biodegradation of toluene in the recycle liquid of biotrickling filters requires the presence of suspended biomass. Hence, the influence of key operating conditions on the concentration of suspended biomass in the recycle liquid was determined. The results presented in Fig. 3 show that high suspended biomass concentrations (measured as total carbon) were only observed at a high toluene inlet concentration in combination with a continuous supply of nutrients.

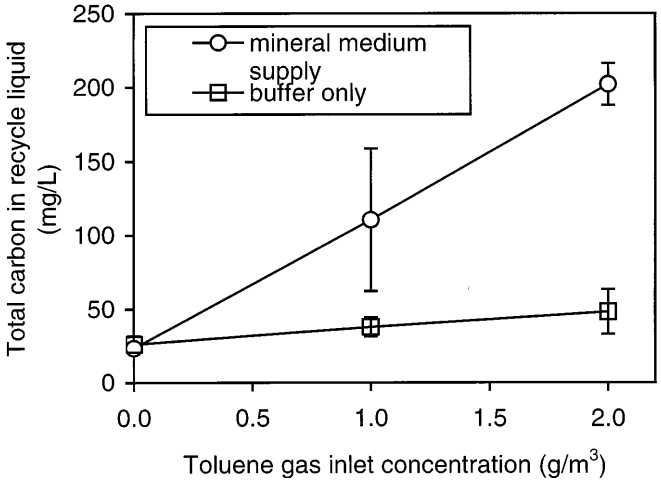

Fig. 3 Influence of the toluene gas inlet concentration during continuous supply of mineral medium or continuous supply of nutrient-deficient buffer solution on steady-state total carbon concentrations in the recycle liquid of a conventional biotrickling filter; *bars* show standard error

Discussion

Only a few reports acknowledge that pollutant degradation in the recycle liquid of biotrickling filters for air pollution control is a relevant process. In two instances, quantification of this process was extrapolated from separate batch culture experiments with suspended biomass. Hartmans and Tramper (1991) estimated a dichloromethane degradation rate of 9.5 g m^{-3} h^{-1} in the recycle liquid in a biotrickling filter with a maximum overall EC of 200 g m^{-3} h^{-1}. Similarly, Okkerse et al. (1999) operated a biotrickling filter fed with a mixture of 80 and 30 g m^{-3} h^{-1} of dichloromethane and methylmethacrylate, respectively, and concluded that the potential for degradation in the recycle liquid was 4.6 g m^{-3} h^{-1} dichloromethane and 820 g m^{-3} h^{-1} methylmethacrylate. However, extrapolation of shake flask experiments may not always be reliable, since the actual activity in the recycle liquid during biotrickling filter operation, i.e., including mass transfer, substrate axial gradients, etc., may greatly differ from the activity under shake flask conditions.

The present study demonstrates the importance of pollutant biodegradation by microorganisms suspended in the recycle liquid of biotrickling filters. During start-up, a short phase of high biological activity in the recycle liquid caused an increase of the overall EC of approximately 65 g m^{-3} h^{-1} (Fig. 1). During prolonged operation, toluene degradation in the recycle liquid contributed up to 21% to the overall EC, or an equivalent of 9.7 g m^{-3} h^{-1} (Table 1). It should be noted that the latter value is the actual rate by suspended biomass during biotrickling filter operation, as determined by removal of suspended biomass from the recycle liquid.

The fact that total carbon in the recycle liquid remained constant for over 4 h during the circulation of water (Fig. 2) indicates that the suspended biomass in the recycle liquid does not originate from biofilm detachment as suggested by Okkerse et al (1999). Rather, it is the result of growth in suspension and is favored by high nutrient and pollutant loadings as shown in Fig. 3. This is supported by the fact that high suspended biomass concentrations were observed before the biofilm had formed, and are reported for day 2 in Fig. 1.

Pollutant biodegradation in the recycle liquid of biotrickling filters is generally neglected because the amount of suspended biomass is very small compared to the amount of immobilized biomass (Table 1). However, the activity of the biomass should be taken into account. Our calculations show that during steady-state operation, the average specific activity of suspended biomass is about 20 times higher than that of the immobilized biomass. The low average activity of immobilized biomass is probably due to a high fraction of inactive or dead biomass combined with oxygen, nutrient, and/or pollutant diffusion limitation commonly reported in biofilm literature. Suspended cells probably face

conditions that are much more favorable. Also, one can further speculate that because of the existence of a continuous liquid purge, selective enrichment of fast-growing organisms occurs in the recycle liquid. This is not the case in the biofilm, where attachment allows retention of slower-growing microorganisms.

Biodegradation in the recycle liquid depends on many factors, such as nutrient supply, liquid residence time, liquid to packed bed volume ratio, and biokinetic parameters of suspended and immobilized cultures. These will be different for every biotrickling filter and one should be careful about generalizations. Still, a short liquid residence time with ample supply of nutrients should maximize the activity and growth in the recycle liquid. This might prove beneficial to temporarily or continuously enhancing the performance of biotrickling filters for air pollution control. In this context, it is interesting that some authors have proposed intermittent trickling in order to improve the mass transfer of hydrophobic compounds to the biofilm (Wolff 1992; De Heyder et al. 1994). The results of the present study suggest that the benefits of intermittent trickling may be offset by lower pollutant degradation in the recycle liquid.

Overall, the present results speak in favor of reactors that solely or partially rely on suspended cultures in a continuous or dispersed liquid phase. Biowashers and airlift bioreactors have indeed shown superior volumetric elimination capacities to biotrickling filters, but so far their use has been restricted to the treatment of relatively hydrophilic pollutants (Van Groenestijn and Hesselink 1993), and airlift bioreactors seem to compare unfavorably when economic considerations are taken into account (Zuber et al. 1997). Even so, the results presented here suggest that the full potential of vapor phase bioreactors relying primarily on growing suspended cultures has not yet been fully explored.

Acknowledgements This project was supported by the US Environmental Protection Agency, project R825392–01–0.

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