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Treatment of Methyl *tert*-Butyl Ether Vapors in Biotrickling Filters. 2. Analysis of the Rate-Limiting Step and Behavior under Transient Conditions

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Detailed experiments were performed with gas phase biotrickling filters treating vapors of methyl *tert*-butyl ether (MTBE), a gasoline additive of great environmental concern. A particular emphasis was placed on the analysis of the rate-limiting step, and it was found that the process was mostly limited by the biological reaction rather than by mass transfer. Further experiments involved the study of the dynamic behavior of the biotrickling filters under simulated field conditions. In all cases, the biotrickling filters adapted rapidly to the new conditions, and new steady states were obtained within hours. The relevance of the results and the implications as far as implementation of biotrickling filters for field MTBE treatment are discussed.

Introduction

The rapidly rising number of reports of groundwater contaminated with the gasoline additive methyl *tert*-butyl ether (MTBE) has raised concerns about its biodegradability. Until about 5 years ago, MTBE was thought to be biologically recalcitrant. However, recent reports have demonstrated that specialized aerobic cultures can degrade MTBE relatively rapidly in the laboratory under well-controlled conditions (*1*−*8*). Even so, clear evidence of MTBE biodegradation in the subsurface is still lacking. This is in part because of the slow rates of MTBE biodegradation, because of its high mobility in the subsurface, and because of the difficulty to close a mass balance in a complex environment.

The physicochemical properties of MTBE pose a challenge for cost effective treatment, and the choice of available techniques for the treatment of MTBE-contaminated streams is limited. In part 1 of this paper (*8*), we reported on the successful enrichment of a consortium capable of completely biodegrading MTBE to carbon dioxide and on the deployment of this consortium in gas phase biotrickling filters. To our knowledge, this was one of the first reports of a successful biotreatment process capable of removing high loads of MTBE. Part 1 focused on microbiological aspects of the process culture and on the steady-state performance of the MTBE degrading biotrickling filters. In the present paper, the steps limiting the rate of treatment are presented and discussed. This is an important procedure which has often been overlooked. This is unfortunate since a clear understanding of the rate-limiting step(s) is a necessity for accurate reactor control and for process optimization. Another important operating aspect which is discussed in this paper is the transient behavior of the biotrickling filters. In the field, transient operation is the rule rather than the exception, and this has been shown to have both short- and long-term implications (*9*−*11*). In the case of MTBE treatment in biotrickling filters, the long startup phase discussed in part 1 raised the question of the ability of the bioreactors to treat effluents with changing conditions. Thus the dynamic behavior of the MTBE degrading biotrickling filters was investigated under selected conditions.

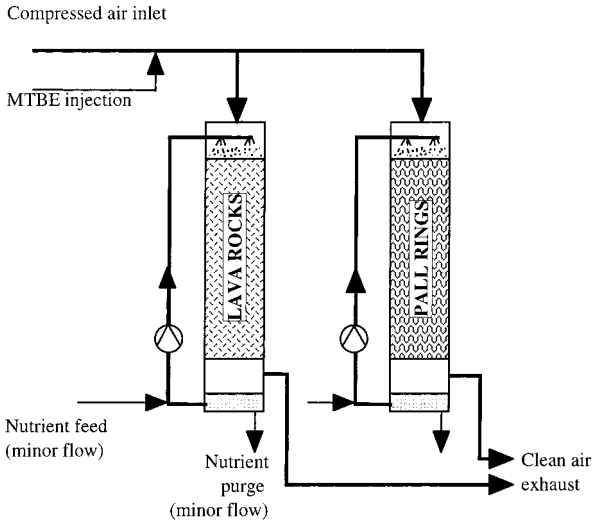

FIGURE 1. Schematic of the experimental setup.

Materials and Methods

Biotrickling Filter Setup and Operating Conditions. Two similar laboratory-scale biotrickling filters were operated in parallel to investigate the removal of MTBE from synthetic waste air streams. A schematic of the experimental apparatus is shown in Figure 1, and details of the experimental methods are described in part 1 of this paper (*8*). In summary, the biotrickling filters were 1.5 m in height and 0.153 m in internal diameter. The height of the packed beds was 0.5 m, and the bed volume was 9 L. Reactor 1 was filled with 8.81 kg of wet lava rock (1−3 cm diameter), and reactor 2 was filled with 0.94 kg of 2.5 cm polypropylene Pall rings (Flexirings, Koch Engineering, Wichita, KS). The initial porosity for the lava rock bed (reactor 1) was 50%, but its surface area was unknown. The Pall ring biotrickling filter (reactor 2) had an initial bed porosity of 90% and a specific surface area of 206 $m^2\ m^{-3}$. A synthetic waste air was produced by injecting a metered flow of MTBE directly into a metered air stream prior to the reactor. Gas and recycle liquid (8.2 $m\ h^{-1}$) flowed concurrently. A constant volume of 3 L of recycle medium was maintained at the bottom of each reactor, and fresh mineral medium (see part 1 for composition) was continuously fed at an average flow rate of 50 $mL\ h^{-1}$ to each reactor. The dynamic liquid holdup in the biotrickling filter was approximately constant at 0.8 L. Each biotrickling filter was inoculated with samples from MTBE-contaminated sites (*8*) and required several months before effective removal of MTBE occurred.

Analysis of liquid and gaseous grab samples for MTBE and potential metabolites was by gas chromatography with a flame ionization detector. Carbon dioxide production was

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TABLE 1. Experimentally Determined Values for the Dimensionless Henry's Law Coefficient (± standard deviation) for MTBE

	air−mineral medium	air−biofilm
Henry coefficient (−)	0.031 ± 0.001	0.023 ± 0.004
temperature (°C)	23.5−23.7	20.5−21.3
MTBE gas concentration (g m^{-3})	0−7	0−20

measured by gas chromatography with a thermal conductivity detector (*8*).

Determination of MTBE Air−Mineral Medium and Air−Biofilm Partition Coefficients. Henry's law coefficients for MTBE were determined experimentally for air−mineral medium as well as for air−biofilm partition as follows. First, 2−3 mL of mineral medium or of slurried acidified biofilm from a toluene degrading biotrickling filter was injected into 40 mL EPA vials with Teflon-lined caps. A known amount of MTBE was then injected into the vials, and the vials were allowed to equilibrate at 21−24 °C for 30 min to 3 h, after which both phases were analyzed for MTBE by gas chromatography as described previously (*8*). Multiple determinations were performed.

Definitions and Performance Reporting. The biotrickling filter performance was reported as the elimination capacity (EC, see eq 1) as a function of the inlet and outlet gas concentrations ($C_{g,in}$, $C_{g,out}$), the air flow rate (Q), and the bed volume (V). The elimination capacity represents the amount of substrate degraded per unit of trickling filter volume, and time and is often reported as a function of the pollutant loading L (eq 2).

$$EC = \frac{(C_{g,in} - C_{g,out})Q}{V} \qquad (g\ m^{-3}\ h^{-1}) \qquad (1)$$

$$L = \frac{C_{g,in}Q}{V} \qquad (g\ m^{-3}\ h^{-1}) \qquad (2)$$

Results and Discussion

Analysis of Rate-Limiting Step. Throughout the experiment, analysis of MTBE in the recycle liquid was performed. These data served three purposes: (1) to determine the amount of carbon leaving the system via the liquid purge and enable closure of the carbon balance; (2) to determine whether the liquid purge contained metabolites that could cause an environmental threat; (3) to determine whether mass transfer or biological reaction was the rate-limiting step of the process. Regarding the latter point, it should be emphasized that various models exist to describe mass transfer of a pollutant from the gas phase to the active biofilm (*12*−*16*). The simplest concept assumes that a liquid layer flows on top of the pollutant degrading biofilm and that the pollutant must fully penetrate the liquid layer before reaching the biofilm. Thus it neglects direct gas−biofilm mass transfer which may play an important role. On the basis of this concept, Pedersen and Arvin (*15*) and Lobo et al. (*16*) discussed the meaning of the respective outlet gas concentration and the recycle liquid concentration at the bottom of the reactor (in the case of concurrent flow). Lobo et al. (*16*) defined a global effectiveness factor $\eta_o = HC_L/C_g$ where C_g is the gaseous concentration and C_L and H are the liquid concentration and the Henry coefficient of the pollutant being treated, respectively. The effectiveness factor varies from 0 when gas−liquid transfer is limiting to 1 when the limitation is in the biofilm. In the latter case, η_o alone does not allow one to determine if the limitation in the biofilm is a kinetic limitation, a liquid−biofilm mass transfer limitation, or a diffusion limitation in the biofilm. To distinguish between these cases, further data on either the rate of biodegradation or on mass transfer and diffusion are required. Even so, the global effectiveness factor is a useful tool to discuss the rate-limiting step(s) in biotrickling filters. Clearly the effectiveness factor will be a function of the operating conditions (gas and liquid flow rate, pollutant concentration), of the biodegradability and diffusivity of the pollutant treated, and of the position in the reactor. For example, it is very possible that gas−liquid transfer will be the rate-limiting step near the air inlet, that the biology will control the rate in the middle of the reactor, and that the rate will controlled by diffusion in the biofilm near the outlet of the reactor.

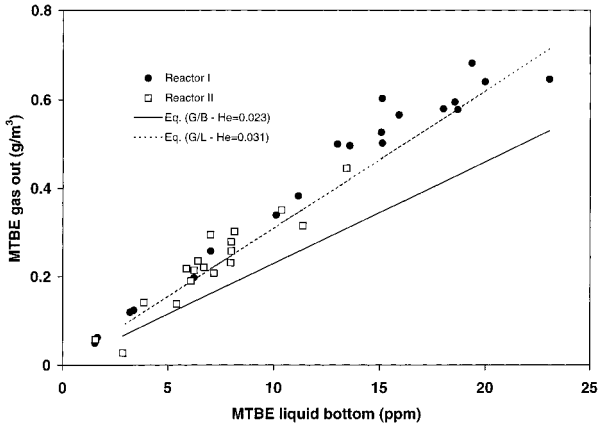

FIGURE 2. Comparison of gas and liquid phase concentrations of MTBE at the bottom of the column (exit ports) and gas−liquid and gas−biofilm equilibrium data for MTBE.

A fundamental parameter for the analysis of the rate-limiting step in biotrickling filters is the Henry's law coefficient of the pollutant undergoing treatment which determines the availability of the contaminant in the liquid phase and in the biofilm. It was determined experimentally in the present study. The average dimensionless Henry coefficients obtained for air−biofilm and air−mineral medium are reported in Table 1. Even if these values are consistent with those reported previously for air−water (0.02 to 0.035 (*17*)), the difference between air−medium and air−biofilm stresses the effect of organic material on partition coefficients. At equilibrium for a given gas phase concentration of MTBE, the biofilm will have a greater MTBE concentration than the scrubbing liquid. This effect is expected to be more pronounced for more hydrophobic pollutants which will have a tendency to preferably partition into the biofilm. This may explain why some very hydrophobic compounds are well removed in biofilters or biotrickling filters although their Henry's law coefficient would predict a relatively low removal performance.

Data for the gaseous and liquid concentrations of MTBE in our biotrickling filters are shown in Figure 2 and compared to equilibrium values based on experimentally determined Henry's law coefficients. Both gaseous and liquid concentrations were measured at the bottom of the bioreactor (outlet ports). Not unexpectedly, the concentration of MTBE in the recycle liquid correlated linearly ($r = 0.96$) with outlet gas phase concentration. However, most outlet gas concentrations were slightly higher (5−20%) than the corresponding equilibrium concentrations. Still, the fact that both phases were close to equilibrium indicates that in our reactors, gas−liquid transfer was fast and that the elimination of MTBE was predominantly controlled by biofilm phenomena. Further, it is interesting to note that even at low gas concentrations, liquid concentrations were never zero, which would have indicated some mass transfer limitation at low concentration. This is probably specific to our MTBE degrading

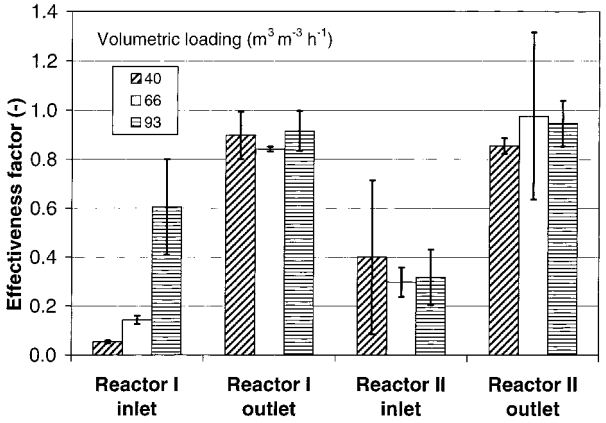

FIGURE 3. Average effectiveness factors $\eta_o = HC_L/C_g$ at the top (air inlet) and at the bottom (air outlet) of the biotrickling filters as a function of the volumetric loading. Since the liquid concentration measured was that of the recycle liquid, the Henry coefficient used in the calculation was that for air−mineral medium. The error bars show the standard deviation ($N = 2-16$).

TABLE 2. Biotrickling Filter Performance at Comparable Loadings but Different Inlet Concentrations

reactor	day	EBRT[a] (s)	MTBE inlet concn (g m^{-3})	MTBE load (g m^{-3} h^{-1})	elimination capacity (g m^{-3} h^{-1})
1	avg 62, 63	90	0.99	39.4	37.1
1	avg 66, 68	54	0.66	43.6	36.4
2	57	90	1.28	51.0	45.4
2	82	39	0.68	63.5	41.6
2	avg 60, 61	90	0.96	38.3	35.0
2	67	54	0.66	43.6	34.3

[a] Empty bed retention time.

biotrickling filters (i.e., the insignificant amount of suspended biomass in the recycle liquid and low content of attached biomass) and is accentuated by the high liquid recycle rate (8.2 m h^{-1}). Figure 3 shows average data for the effectiveness factor η_o defined by Lobo et al. (*16*) and determined for both the top of the column (air and liquid inlet side) and the bottom of the column (air and liquid outlet) for the three different air flow rates tested. The data stress the fact that the rate-limiting factor changes throughout the length of the reactor. In the present case, gas−liquid transfer limitation was significant at the top of the column (inlet port) as indicated by low effectiveness factors. This was expected, however, as modeled by Diks and Ottengraf (*18*), Zuber (*19*), or Barton et al. (*12*). Bulk gas and liquid concentrations rapidly reach values close to gas−liquid equilibrium in systems where gas−liquid mass transfer is faster than biodegradation. Therefore, effectiveness factors close to 1 are observed at the bottom (outlet port) of both reactors. Certainly, outlet values are a good representation of the effectiveness factor throughout most of the height of the reactors.

Overall, the data of Figures 2 and 3 demonstrate that the performance of both reactors was limited by biofilm phenomena, i.e., either liquid−biofilm transfer, diffusion in the biofilm, or biodegradation in the biofilm. As stated above, the effectiveness factor alone does not allow one to distinguish which one of the biofilm phenomena is rate-limiting. A detailed comparison of MTBE elimination data at different concentrations but at similar loadings (Table 2) reveals that the pollutant elimination was virtually unchanged by concentration changes. This indicates that biodegradation rather than mass transfer was the rate-limiting step in the biofilm, since both the diffusion rate and liquid−biofilm mass transfer

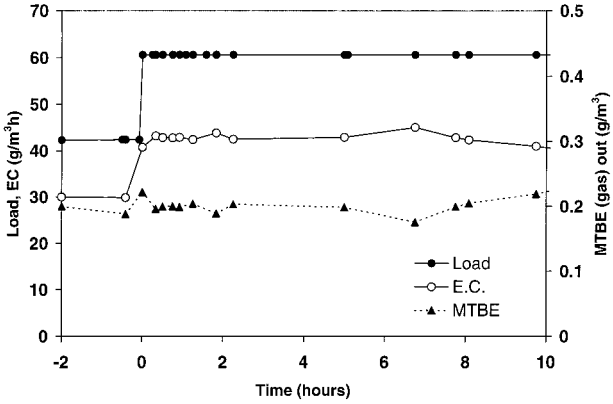

FIGURE 4. Dynamic response of the biotrickling filter packed with lava rocks to a step in the air flow rate at constant MTBE inlet concentration (0.65 g m^{-3}). Initially, the empty bed retention time was 54 s, and at time zero it was lowered to 39 s.

are dependent on the concentration. If diffusion or liquid−biofilm transfer was limiting, the concentration increases listed in Table 2 would have resulted in higher elimination capacities. The observation of a biological limitation is consistent with the relatively low biomass content in the reactors and with the relatively slow rate of MTBE biodegradation compared to other VOCs.

In general, biotrickling filters operating under biological limitation are more difficult to operate than those limited by mass transfer. This is because performance will be highly susceptible to fluctuations in biological activity. Consequently, optimization of MTBE removal in biotrickling filters should consider strategies to establish and maintain a high density and a high specific activity of the process culture. Clearly, effective inoculation with MTBE degraders is warranted. This may pose a challenge, as the present knowledge about MTBE degrading organisms is still relatively limited. Maintaining a stable and effective process further requires a thorough control of cell density, of operating and environmental parameters (nutrients, dissolved oxygen, pH, temperature, inhibitory byproducts), and of the ecology of the biofilm (culture composition, presence of predators such as protozoa, viruses, etc.). While the former parameters are easy to monitor and control in bioreactors equipped with some degree of instrumentation, fundamental knowledge for the proper management of culture ecology is still lacking.

Dynamic Behavior of the Biotrickling Filters. In the field, bioreactors for air pollution control are exposed to continuously changing conditions rather than to constant air flow and steady concentrations. This has shown to affect pollutant removal performance (*9*−*11*); therefore, the transient response of the MTBE degrading biotrickling filters was studied. Two typical responses were investigated: a step up in the air flow rate while keeping the inlet MTBE concentration constant, and a step up in the inlet MTBE concentration while keeping the air flow rate constant.

Figures 4 and 5 present the results of the first step change where the air flow rate was increased. The data show that as far as reactor performance is concerned, a new steady state was rapidly established, within 2 h. This was a slight surprise since, usually, operation with hydrophilic compounds can require up to 10−20 h to reach a steady state after a concentration step change, simply to reach a new gas−liquid equilibrium (*9*−*11*). Of course, the duration of any transition is always dependent on the reactor conditions and on the support material (e.g., presence of activated carbon). Further, because of the sensitivity of MTBE degrading cultures to stress and changes in environmental conditions, an adaptation time for the process culture or even a temporary inhibition was expected. This was not the case; the present results show

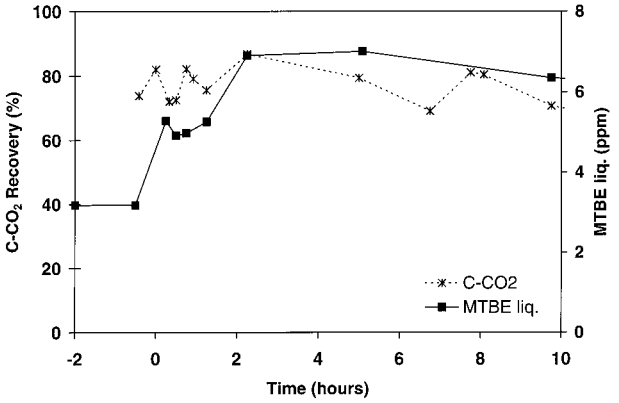

FIGURE 5. Liquid concentration and recovery of C-MTBE degraded as C-CO_2 after a step change in air flow rate. Conditions as in Figure 4.

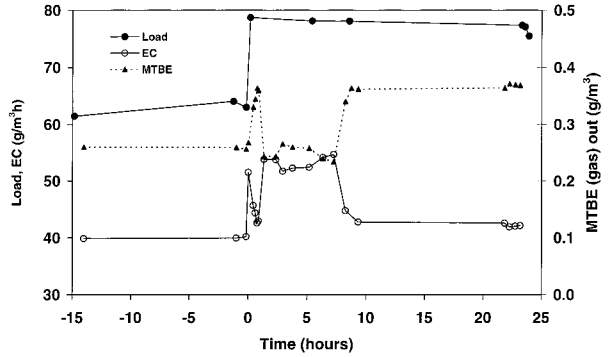

FIGURE 6. Dynamic response of the biotrickling filter packed with lava rocks to a step in the inlet concentration of MTBE at a constant empty bed contact time of 39 s. Initially, the inlet MTBE concentration was 0.66 g m^{-3}, and at time zero it was raised to 0.82 g m^{-3}.

that a very fast acclimation of the process culture to new conditions occurred. The increase in elimination capacity after the step change indicated that, originally, the reactor was operated in the first-order regime, where the elimination capacity is a function of the loading. After the step, the reactor reached a performance close to its maximum elimination capacity (42 g m^{-3} h^{-1}). Throughout the experiment, the recovery of the degraded carbon-MTBE as carbon-CO_2 remained high (Figure 5), which indicates that sorption was not a major removal mechanism during the step change. This explains in part why a new steady state was rapidly established. In good correlation with the duration of the transient phase, the concentration of MTBE in the recycle liquid increased from about 3 to 6 mg L^{-1} after the step change. This increase in MTBE liquid concentration was probably the driving force for the increase in elimination capacity after the step change, as the degradation kinetics had not reached saturation prior to the step change. Overall, the concentration of MTBE in the liquid phase remained below 10 mg L^{-1} throughout this and all other experiments. This indicates that, even during step changes, the absolute amount of MTBE leaving the system via the liquid purge is insignificant. It always remained between 0.02% and 0.18% of the MTBE fed to the system, and the amount purged would not pose any problem if field implementation was considered.

Figures 6 and 7 report the transient behavior of the biotrickling filter packed with lava rocks after a step change in the inlet concentration of MTBE at a constant empty bed retention time of 39 s. During the first 60 min after the step change, a short absorption phase took place which temporarily resulted in a high elimination capacity (Figure 6). Unfortunately, the frequency of sampling for liquid analysis did not allow the monitoring of a corresponding concentration increase in the liquid phase. Thereafter, the biotrickling filter dynamic response showed an unexpected behavior. MTBE outlet concentrations decreased to levels comparable to those prior to the step and remained constant for about 6 h, and finally they increased again to reach values close to those found 1 h after the step change. This unexpected pattern is consistent with the time course of the liquid concentration of MTBE (Figure 7) and was well beyond experimental fluctuations. During this 6 h phase, high elimination capacities (Figure 6) were observed, and the recovery of the degraded MTBE as carbon dioxide exceeded 100% (Figure 7), which indicates that the process culture was simultaneously degrading other carbon sources available in the reactor (biofilm polymers, dead cells, or other nonvolatile dissolved carbon sources). One can speculate that this was a factor for the temporary high performance of the reactor and that when these sources of carbon were depleted, the reactor returned to a new steady state. Another speculative explanation for the observed response is that the process culture was under a significant stress after the step increase in inlet MTBE concentration, and until it adapted to the new conditions, it was very active in degrading the additional MTBE in order to be relieved from the stress. Such stress responses are remarkably poorly understood, but have been suggested in other applications. Further studies would be necessary to validate either of the above hypotheses. However, it is interesting to speculate that significant performance improvement could possibly be achieved by subjecting the process culture to selected repeated stresses or by supplying the process culture with an alternate carbon source.

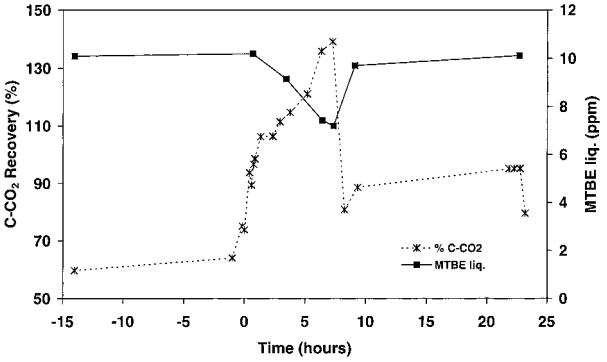

FIGURE 7. Liquid concentration and recovery of C-MTBE degraded as C-CO_2 after a step change in air flow rate. Conditions as in Figure 6.

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