

Transient-State Behavior of a Biofilter Removing Mixtures of Vapors of MEK and MIBK from Air

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In the work reported here, selected aspects of the dynamic behavior of biofilters for waste air treatment have been investigated. Emphasis was placed on transient state elimination of mixtures of methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK) vapors and on explanation of the observed phenomena. The initial startup, the response of the biofilter to step changes in the pollutant loadings, responses to pollutant pulses, restarting after starvation, and the influence of step changes in gaseous phase oxygen partial pressure are presented and discussed. © 1996 John Wiley & Sons, Inc.

Key words: gas phase bioreactor • dynamic behavior • waste air • MEK • MIBK

INTRODUCTION

Dynamic behavior has been extensively studied in many types of bioreactors. However, for biofilters and bioscrubbers for waste air treatment, virtually nothing has been published, despite an essential need to obtain reliable information about the response of such bioreactors to either perturbations or changes in their operating conditions in order to ensure effective performance.

Biofilters are those bioreactors in which a mixed culture is attached to a stationary support material such as compost, soil, peat, or activated carbon, and direct contact occurs between the attached microbial film and the humid pollutant containing waste gas stream undergoing treatment. Biofilters are a major advance in environmental protection. They offer cost-effective treatment for volatile organic compounds (VOCs) and odor elimination from waste air, particularly when high flow rates and dilute streams are involved.

Biofilters operating in industry are generally exposed to a spectrum of changing conditions, particularly when assigned to the treatment of waste air from discontinuous processes. In the chemical industries, the most common sources of variation in the waste air composition and flux are weekly rotations in the production. In addition, extreme variations in waste air composition and

flux also result from reactor washing and accidental spillages. Accordingly, typical operating conditions for biofilters are essentially a sequence of changes, stationary conditions, and interruptions that will affect their overall performance. This emphasizes the importance for obtaining reliable information on the behavior of biofilters for waste air treatment under real conditions, i.e., under unsteady-state conditions.

The steady-state operating characteristics of biofilter have been widely investigated. However, only minor attention has been given to transient-state performance and the phenomena occurring during changes and interruptions.^{1,6,16} Clearly, in-depth studies of transients in biofilters are required in order to provide the basic empirical knowledge necessary for plant design, scale-up, and performance determination under real conditions. In addition, transient studies offer a genuine basis for the development of a conceptual explanation of the complex phenomena that occur in biofilters during pollutant elimination, thereby providing an opportunity for further progress in establishing fundamental understanding of such reactors.

The present work establishes a general framework concerning the dynamic behavior of biofilters for waste air treatment. The initial startup period is described, and transient responses of the types most likely to be encountered in biofilter operation are investigated and explained. In addition, the influence of oxygen partial pressure and of a starvation period is discussed. Mixtures of methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK) vapors, two common solvents extensively employed in industry and major components of paints and varnishes, served as model pollutants for this study.

MATERIAL AND METHODS

A schematic diagram of the equipment used is shown in Figure 1.

Biofilter and Packing Material

The biofilters were constructed from acrylic glass tubing and were 1 m in length and 80 mm in internal diameter

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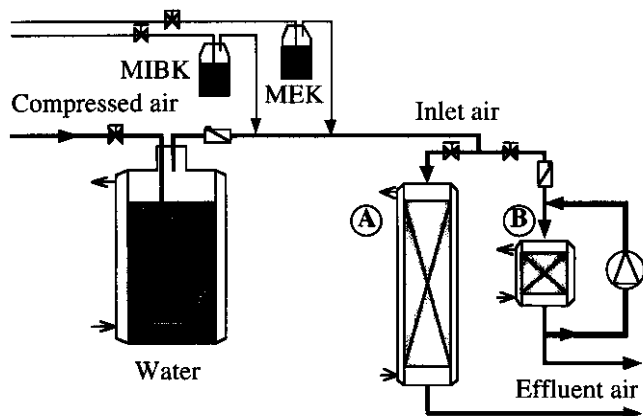


Figure 1. Schematic of the equipment used: (A) conventional biofilter (one air pass); (B) differential biofilter: part of the effluent air is recycled to the inlet in order to establish a differential mode.

for the conventional biofilter and 0.35 m in length and 81 mm in internal diameter for the differential biofilter. Column temperatures were maintained between 20 and 25°C with electrical thermostatic jackets.

The biofilters were filled with Bioton,® a commercially available biofilter packing (ClairTech, Utrecht, The Netherlands), comprising an equivolume mixture of compost and polystyrene spheres. Acid neutralizing components (primarily limestone) were also included in the biofilter material, but no activated carbon was incorporated. The voidage of the packing material, determined by studying the residence time distribution after a pulse of inert gas, was 50%.⁶ The active filter bed height was between 0.8 and 0.95 m for most experiments with the conventional biofilter and 0.2 m for the differential biofilter. The packing density (60 wt % water content) was between 220 and 330 g of packing per liter of bed volume. Before use, the packing material was inoculated with a concentrated enrichment culture. No additional mineral nutrient source or pH buffer was added after beginning the experiments.

Inoculum

Ketone degrading enrichment cultures were grown in a mineral medium with MEK, MIBK, or mixtures of MEK/MIBK as sole carbon and energy substrate(s) with regular transfers. The initial source of microorganisms was from samples from several wastewater treatment plants and soils. Samples subjected to high levels of aeration were preferred. The enrichment cultures showed extensive growth on either MEK and MIBK or mixtures of the two substrates. The packing material inoculum was prepared by concentrating 3 L of enrichment culture to 0.02 L by centrifugation. This was sufficient to coat 1 kg of packing material prior to its introduction into the columns.

Pollutant Containing Humid Air Stream

Compressed oil-free air was saturated with water vapor by sparging the air through a 50-L bottle containing

deionized water thermostated at 28°C. Two smaller compressed air streams were sparged into 0.5-L bottles, containing either MEK and MIBK as required, and subsequently mixed with the major humidified air stream. The main air stream was regulated by mass flow meters (Brooks, the Netherlands). Nonreturn valves were installed in order to prevent contamination of the humidifying section with pollutant vapors. A metered flow of pollutant-containing humid air was passed downward through the biofilters.

For establishing the differential biofilter, recycling of part of the effluent air was achieved with a magnetic pump (Reciprotor, Copenhagen, Denmark) at a constant flow rate of 720 L h⁻¹, which was more than 10 times the net maximum inlet flow rate tested, allowing axial gradients to be neglected in this reactor.

Operating Conditions

Downward gas flow rates of 0.2, 0.3, or 0.4 m³ h⁻¹ were used in most experiments, giving surface loadings of 40, 60, or 80 m h⁻¹ and volumetric loadings of 44, 66, or 88 h⁻¹, respectively. The gas had a relative humidity greater than 95%, and the pressure drop over the filter was less than 50 mm water gauge.

Analysis

The concentrations of MEK and MIBK in the gas phase were determined by gas chromatography. Polluted air was pumped through 0.1-mL sampling loops for automatic injection into a Hewlett-Packard type 5890A gas chromatograph fitted with a 15m HP-50+ column and operated isothermally at 45°C. The carrier gas used was helium (2.25 L h⁻¹) and detection was with a flame ionization detector. The detection limit was a ca. 5 mg pollutant per cubic meter of air. The use of known air flow rates and both MEK and MIBK mass flow rates allowed the calibration of both systems. The retention times were 0.7 and 1.7 min for MEK and MIBK, respectively. Neither metabolites nor MEK or MIBK degradation by-products other than carbon dioxide were ever detected.

RESULTS AND DISCUSSION

Startup Period

Remarkably few publications report details concerning the startup period of biofilters. This is probably either because of its relative irrelevance compared to biofilter lifetime or because starting up is usually thought not to influence the future performances of biofilters. However, optimization of biomass densities through better understanding of biofilm growth in biofilters alter such opinions and, clearly, further research in this area is necessary.^{2,10,13}

Typical data for the startup of a biofilter removing mixtures of MEK and MIBK are shown in Figure 2. After an initial sorption phase of ca. 8 h, the biofilter progressively gained in efficacy, becoming fully effective after 4.5 days. This is fairly rapid compared to startup times that have been reported previously. Furusawa et al.¹² reported that 12 days elapsed before complete removal of 125 ppm hydrogen sulfide was achieved, and Ergas et al.¹¹ reported several weeks before dichloromethane degradation occurred. On the other hand, Togna et al.¹⁷ reported a 3-day biofilter startup period for a pilot scale biofilter degrading styrene. In our case, appropriate inoculation of the packing material with enrichment cultures was probably a major reason for the brevity of the startup. It is most surprising to find MIBK as the first model pollutant to be degraded, particularly as in other biofiltration experiments it was this pollutant that was removed more slowly.⁵⁻⁸ Biodegradation experiments in shaken flasks⁶ showed a similar pattern of behavior. In those experiments, the MEK lag phase was slightly longer than that for MIBK, although during mixed pollutant removal, the MEK degradation rate was significantly higher than that of MIBK.

As shown in Figure 3, the pollutant degraded increased exponentially during the acclimation phase. This indicates an exponential buildup of active biomass and/or expression of the enzymes responsible for the degradation of the ketones. Nonlinear regression of the amount degraded during removal acceleration permitted calculation of the doubling time that corresponded

to a doubling of the elimination capacity. The following doubling times were observed:

MEK	activity doubling time: 0.45 days	$r = 0.996$
MIBK	activity doubling time: 1.04 days	$r = 0.997$

Preliminary results showed that during this phase the extractable nitrogen, i.e., nitrate and ammonium, from the packing material fell to zero. Furthermore, the measured production of carbon dioxide corresponded only to ca. 42% recovery of the carbon entering the system, thus indicating a high yield coefficient for biomass formation.⁴

Cultures extracted from biofilters and grown in shake flasks were studied with respect to their growth rate and biodegradation kinetics.⁶ In liquid culture, the doubling times for growth on MEK and MIBK as single pollutants, calculated for liquid concentrations of 0.23 and 0.1 g L⁻¹ of pollutant (which are the liquid concentrations in equilibrium with the gaseous concentrations utilized during biofilter startup), were 6.6 and 8.2 h for MEK and MIBK, respectively. The significantly longer activity doubling times observed in biofilters reflect environmental effects encountered by microbial populations in such reactors.

Step Change Experiments

The present section deals with some typical responses that may occur in real systems, particularly step changes in pollutant inlet concentration and in air flow rate. Here, experiments were performed in which the air flow

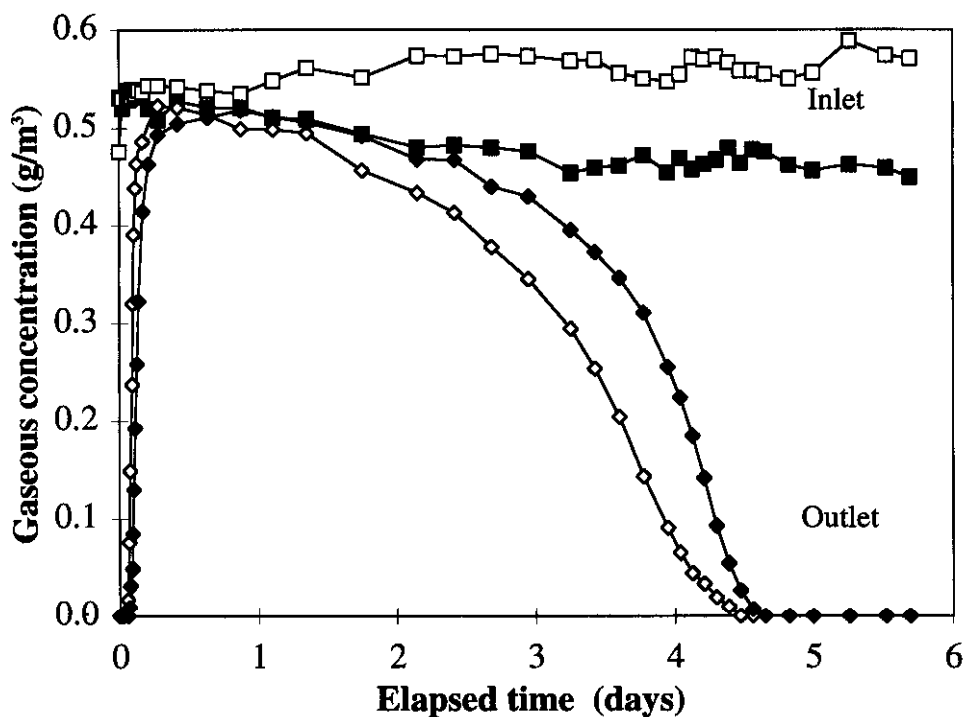


Figure 2. Initial startup time course. At time zero the inlet concentrations of MEK and MIBK were set at 0.53 and 0.56 g m⁻³, respectively. Air flow rate: 200 L h⁻¹ (volume load: 44 m³ m⁻³ h⁻¹). MEK (■, ◆), MIBK (□, ◇).

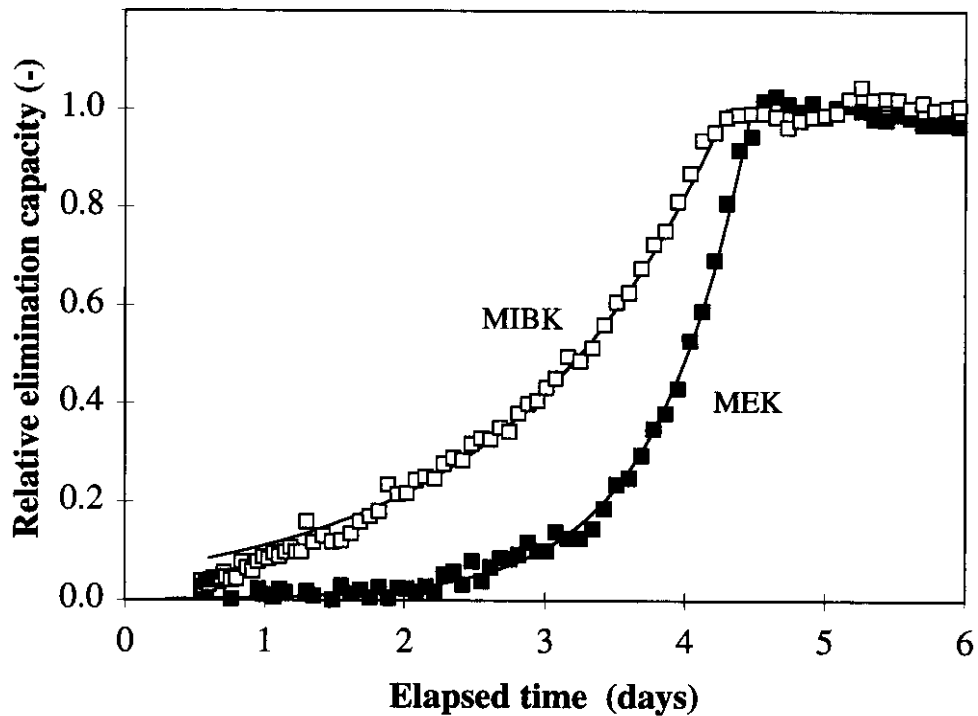


Figure 3. Relative elimination capacity during initial startup. The lines represent the nonlinear regression calculated with measurements between day 1 and the time when full efficiency is reached. For this experiment, a relative elimination capacity of 1 represents 23.3 and $24.6 \text{ g m}^{-3} \text{ h}^{-1}$ for MEK and MIBK, respectively.

rate and/or the inlet pollutant concentration in the inlet air stream were varied stepwise and the transient response of the biofilter examined. Usually, after the step changes, about 2–5 h were needed in order to reach

new stationary conditions. Due to intense sorption onto the packing, a delay of ca. 0.5 h was observed between each step and significant changes in the outlet concentration. However, the phenomena involved during step

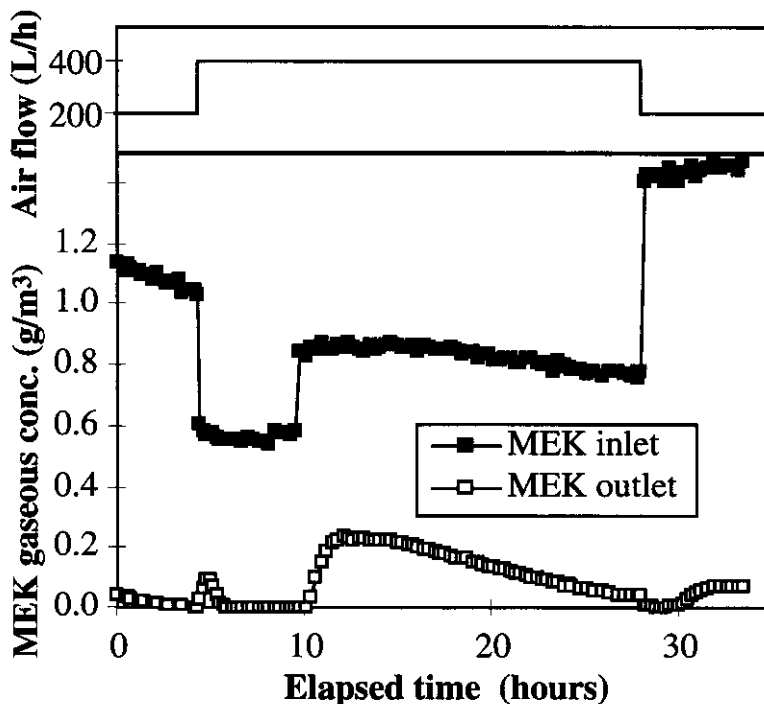


Figure 4. Dynamic response of the biofilter to step changes in both MEK inlet concentrations and air flow rates during MEK removal as single pollutant.

changes have been presented elsewhere⁸ and discussed with respect to the dynamic modeling of biofilters. In summary, the previously reported findings indicate the following.

MEK Step Changes

In the case of MEK, three types of step changes were investigated, one in which the air flow was essentially doubled with approximate halving of the MEK inlet concentration, a second, where at constant air flow rate, the MEK loading was increased by ca. 50%, and finally, an operating situation where the air flow rate was essentially halved so that the MEK inlet concentration essentially doubled relative to its previous level. As shown in Figure 4, the first step change (4 h) resulted in minor breakthrough for a period of approximately 1 h, after which complete elimination was again achieved. The second change (10 h) resulted in significant breakthrough which declined linearly from a maximum some 1 h after the change to ca 0.08 g m^{-3} 18 h after the change. The final step change (28 h) resulted in essentially complete removal for a period of ca. 2 h prior to minor breakthrough and establishment of a steady state.

MIBK Step Changes

In the case of MIBK, changes at essentially constant loading (4, 14, and 19 h) and step increases in MIBK loadings (3, 8, and 22 h) were undertaken, as reported in Figure 5. Because the elimination capacity for MIBK was significantly lower than that for MEK, the experiment occurred close to domain, where the elimination capacity no longer depends on the pollutant loading. The preponderant influence of sorption processes under

the operating conditions investigated resulted in approximately similar breakthrough throughout transient-state operation.

Combined MEK and MIBK Step Changes

Step changes during the removal of mixtures of MEK and MIBK proved complex because of the interdependency of the biodegradation of the two ketones on each other,^{4,6,8} although they reflect real situations. During the experiment shown in Figure 6, both the air flow rate and the inlet concentration of MIBK were kept constant at 200 L h^{-1} and 0.28 g m^{-3} , respectively, while step changes in MEK inlet concentration were performed.

MEK breakthrough was found to occur after the first step change (6 h). A further step increase in MEK inlet concentration at 10 h resulted in an increase in the MEK outlet concentration. Finally, complete removal was re-achieved shortly after the MEK inlet concentration was returned to its initial value (13 h). MIBK removal was increasingly affected by successive increases in the MEK gaseous phase concentration, as shown in Figure 7, where the elimination capacities are reported for both ketones.

Significant increases in MEK elimination capacity were observed to be parallel to the imposed step changes, which indicates that the experiment was performed below the critical loading for the biofilter. Immediately after the first two step changes, sorption onto the packing started to play a major role, and the apparent elimination capacity was enhanced until equilibrium was reached. After the last step, apparent elimination, as strictly defined, is negative because of MEK desorption.

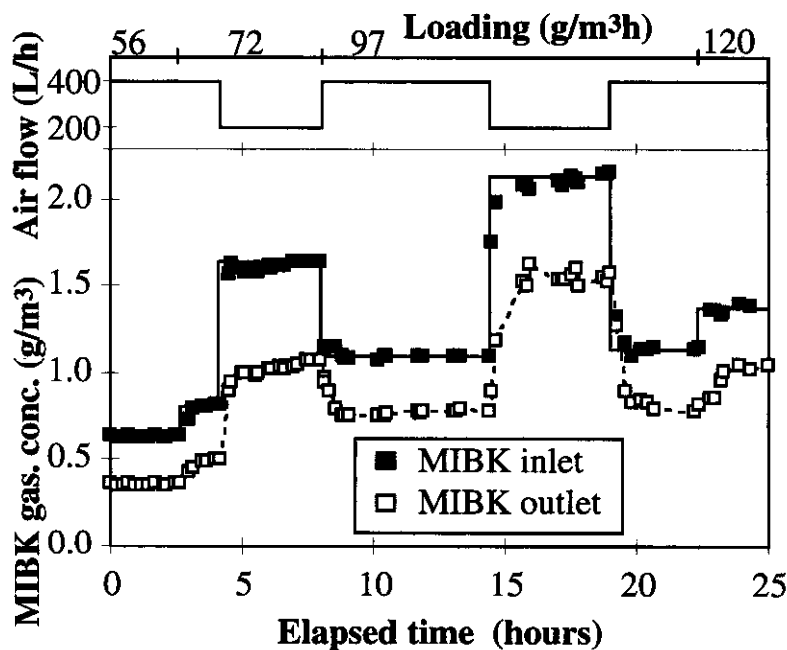


Figure 5. Dynamic response of the biofilter to step changes in MIBK inlet concentration and air flow rate during MIBK removal as single pollutant.

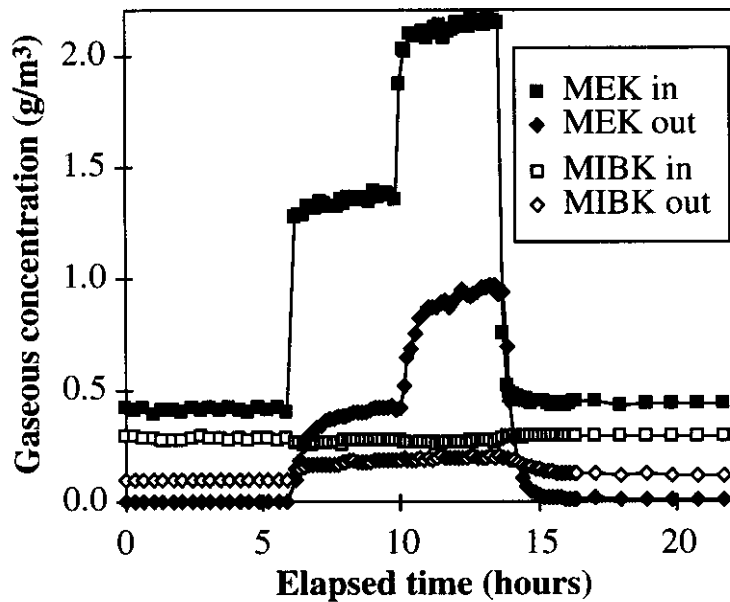


Figure 6. Dynamic response of the biofilter to step changes in MEK inlet concentration during mixed MEK and MIBK removal at a volumetric loading of $44 \text{ m}^3 \text{ m}^{-3} \text{ h}^{-1}$. MEK inlet (■) and outlet (◆); MIBK inlet (□) and outlet (◇).

The importance of sorption effects during step changes was noted previously.^{1,8} MIBK elimination was also found to be markedly influenced by changes in MEK concentrations, and its elimination fell from 8 to $3 \text{ g m}^{-3} \text{ h}^{-1}$ but recovered to its former value within 2 h after the MEK inlet concentration was also returned to its initial concentration. This further emphasized the close interdependency of the biodegradation of the two pollutants used in this investigation and indicates a requirement for more detailed definition of degradation kinetics in biofilters operating with binary and multiple pollutant mixtures.

A similar experiment was performed in which the MEK inlet concentration was maintained constant and MIBK inlet concentration was increased stepwise.^{6,8} Similar cross-inhibition was observed, although to a lesser extent than in the experiment described in Figures 6 and 7.

MEK and MIBK Pulse Experiments

Pulse experiments were performed to study the dynamic response of biofilters to peaks in pollutant concentration of the type that might occur after a process malfunction. A weighed amount of either MEK or MIBK was in-

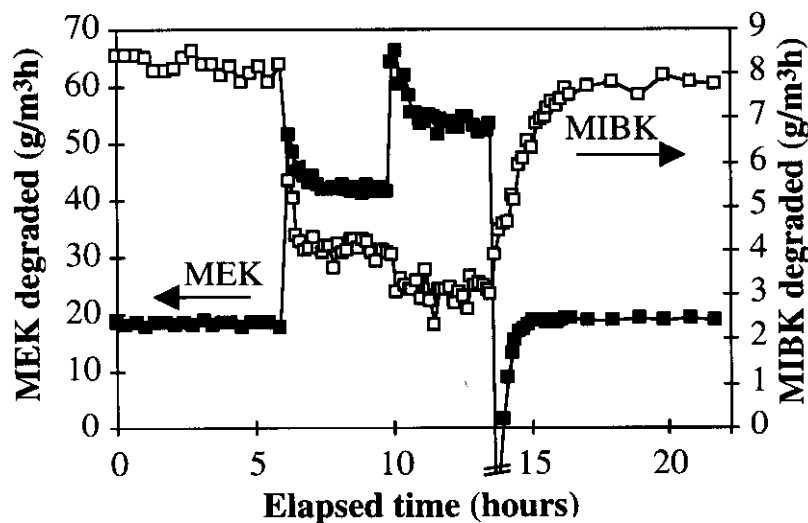


Figure 7. Elimination capacity for MEK (■, left scale) and MIBK (□, right scale) during step changes in MEK inlet concentration.

jected with a syringe onto the top surface of the biofilter bed, where expanded clay spheres ensured its effective evaporation without direct contact of liquid pollutant with the biofilter bed. Both midheight and outlet concentrations were measured in order to follow each pollutant's axial movement through the biofilter bed. At the inlet, the exact time course of the injected pulse could not be measured. No comparison with other results was possible because none concerning the transient response of biofilters to pulse perturbations have been published.

MEK Pulse

In Figure 8 are presented the results from an experiment where the air flow rate was kept constant at 300 L h^{-1} , i.e., a volumetric loading of $66 \text{ m}^3 \text{ m}^{-3} \text{ h}^{-1}$. The base feeds of MEK and MIBK in the inlet air stream were 0.87 and 0.70 g m^{-3} , respectively. After 1 h, an additional quantity of 0.41 g of MEK was injected onto the biofilter surface.

Assuming that the pulse of MEK would last about $2 \pm 1 \text{ min}$, the inlet concentration could have reached $55 \pm 27 \text{ g m}^{-3}$, an extremely high value, and in the upper part of the biofilter, local concentration gradients of MEK could not be excluded. The dynamic response of the biofilter, shown in Figure 8, indicates that the midheight MEK concentration reached 9 g m^{-3} , followed by a rapid decrease. However, at the outlet, the

pulse was markedly attenuated and the outlet MEK concentration never exceeded 1.3 g m^{-3} . Moreover, complete removal of MEK reoccurred some 3 h after the pulse.

MIBK biodegradation was, not unexpectedly, influenced by the MEK pulse, and significant increases in both midheight and outlet MIBK concentrations were observed. No explanation was found for the transient decrease in MIBK midheight concentration immediately after pulsing MEK.

The integration over the time period of both MEK midheight and outlet concentrations permits determination of the amount of pulsed MEK that was degraded. The steady-state concentrations (concentrations previous to pollutant pulse) were taken as baseline values so that integral values and the pulsed amount could be compared.

The following results were obtained for the amount of pollutant present at particular sample ports in excess of the steady-state values:

At midheight: $0.74 \pm 0.25 \text{ g MEK}$
 At the outlet: $0.24 \pm 0.05 \text{ g MEK}$

Integration by the triangular method was rather imprecise at midheight because of a lack of measurements. However, the estimated value of 0.74 g is significantly higher than the amount pulsed (0.41 g), showing that, at the concentrations involved, self-inhibition of MEK biodegradation most probably occurred. Such inhibition

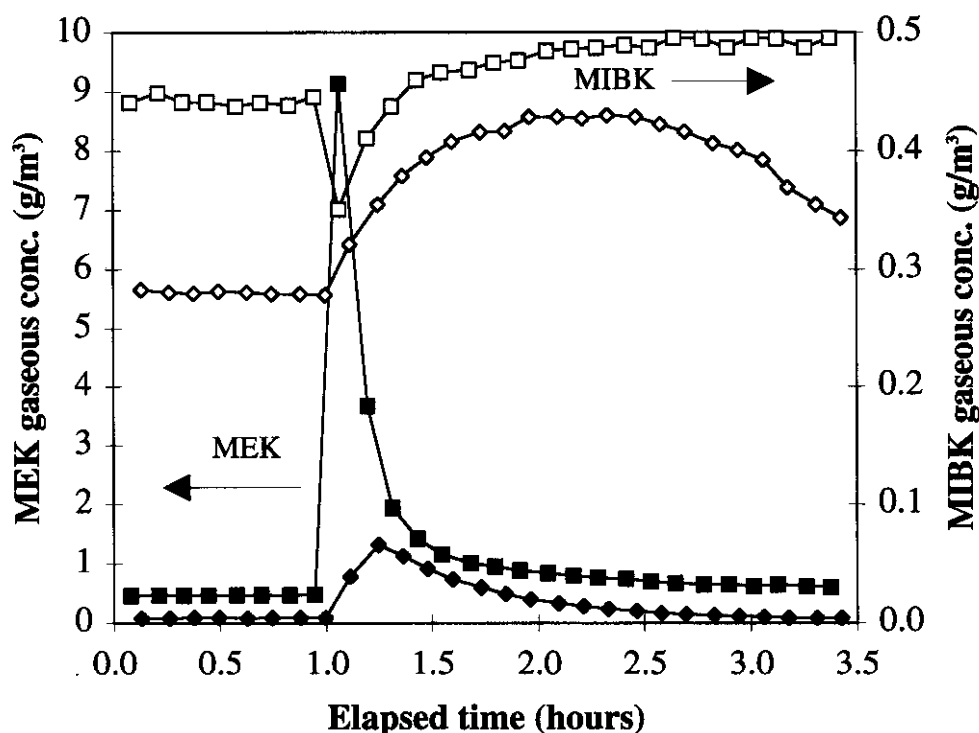


Figure 8. Dynamic response of the biofilter to a 0.41-g MEK pulse in the inlet stream. Midheight and outlet concentrations are reported: MEK (left-hand scale) midheight (■) and outlet (◆); MIBK (right-hand scale) midheight (□) and outlet (◇).

seems not to be rapidly reversed, as a slightly higher midheight concentration occurred at the end of the experiment.

Integration of the outlet concentration showed that 0.17 g out of the 0.41 g of pulsed MEK was eliminated in the biofilter. Considering the time course of MEK at midheight, most biodegradation was achieved in the bottom part of the reactor. This was apparently accomplished at the partial expense of MIBK biodegradation, as indicated by the perturbed MIBK time course, particularly at the outlet, shown in Figure 8.

Significant self-inhibition of MEK biodegradation was also observed in suspended cultures grown in shake flasks,⁶ particularly for liquid concentrations above 0.36 g L⁻¹. The corresponding gaseous equilibrium concentration, based on Henry's law, to that liquid concentration is 0.85 g MEK per cubic meter of waste air. Most importantly, during biofilter operation, no inhibition occurred for such gaseous pollutant concentrations. However, a similar calculation using a MEK liquid concentration of 5 g L⁻¹, which seems more appropriate for describing the MEK acute inhibition threshold in shake flasks (unpublished results), leads to inhibitory gaseous concentration of ca. 12 g m⁻³, which corresponds to concentrations observed during MEK pulse biofiltration experiments.

MIBK Pulse

In a similar manner, 0.39 g of MIBK was pulsed to a biofilter operating under the same conditions as dis-

cussed for MEK. The results, presented in Figure 9, show that both MIBK midheight and outlet concentration undergo a rapid decrease, after first reaching a maximum. This rapid transition is most probably due to both the relatively low solubility of MIBK and its high Henry coefficient ($H_{\text{MIBK}} = 5.7 \times 10^{-3}$, $H_{\text{MEK}} = 2.4 \times 10^{-3}$.)⁶ Consequently, the pulsed MIBK was sorbed to a lesser extent than was MEK in the preceding experiment and, therefore, was rapidly flushed from the system. Integration of the dynamic response confirmed that most of the MIBK pulsed was recovered in the outlet stream from the biofilter.

The following amounts were detected in excess of the steady state concentrations:

At midheight: 0.40 ± 0.15 g MIBK
At the outlet: 0.35 ± 0.05 g MIBK

In this case, almost no effect of the pulsing of MIBK on the biodegradation of MEK was observed. This was surprising, particularly as in all previous experiments a marked influence of MIBK on MEK removal, especially at high loadings, was evident.^{4,8} Here, the process culture seemed to be unaffected by the MIBK pulse. The short exposure time to high MIBK concentrations and the high MIBK Henry coefficient are the most plausible explanations for the absence of inhibition. A certain adaptation time for the process culture to switch from MEK to MIBK degradation could not be excluded.

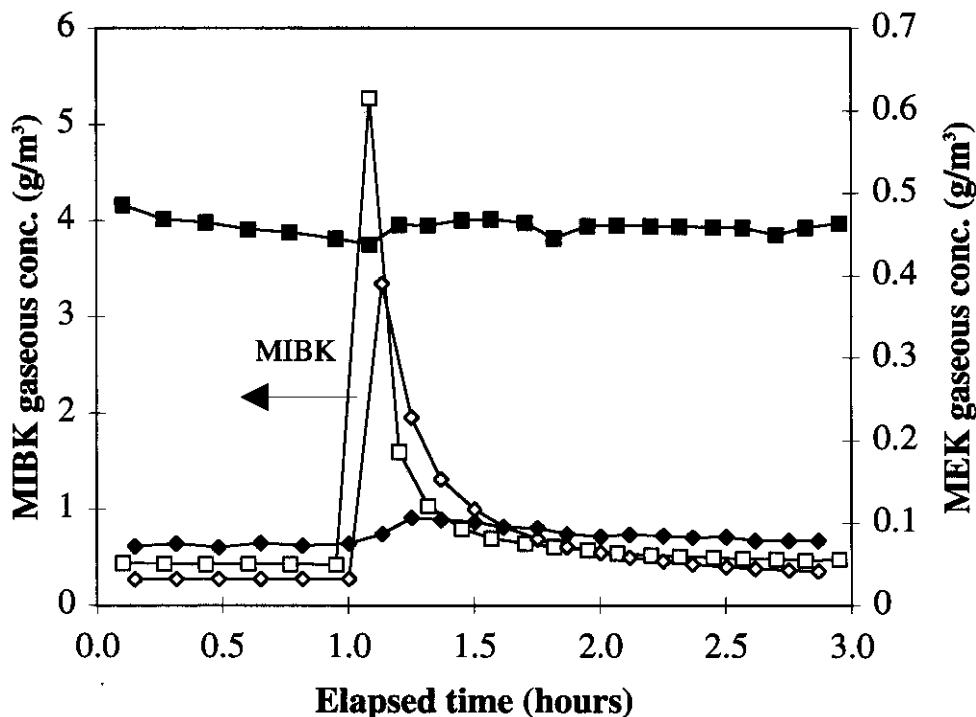


Figure 9. Dynamic response of the biofilter to a 0.39-g MIBK pulse in the inlet stream. Midheight and outlet concentrations are reported: MEK (right-hand scale) midheight (■) and outlet (◆); MIBK (left-hand scale) midheight (□) and outlet (◇).

Starvation Experiment

The influence of starvation on the removal efficiency of the biofilter when restarted was tested in order to determine whether the process culture could stand such situations and, additionally, to define the time needed to recover full efficiency. During this investigation, both the air flow and pollutant supply were interrupted for a period of 5 days, after which the system was restarted under the same conditions pertaining prior to the interruption. Figure 10 shows the time course after the restart on a logarithmic scale. Major differences were observed between the initial startup (see Fig. 2) and restarting after 5 days interruption. In the restarting case, biodegradation already occurs during the sorption phase, with immediate and efficient biodegradation restoration. This is much more rapid than has been reported by Bronnenmeier et al.,³ who found that after an 8-h period of starvation, some 16 h was required before 75–80% recovery of pollutant elimination capacity was achieved. In an airlift bioreactor used for dichloromethane vapor removal, as much as 2 days was required to recover efficient elimination after a 3-day shut-down.¹⁴ The observed apparent gain in removal efficiency after 8–10 h is questionable, as this could either be a consequence of extra biomass reactivation in the biofilter or result from fluctuations in the operating temperature.

The present experiment proves that after a 5-day stoppage, prompt and efficient treatment can readily be reestablished, as far as MEK and MIBK elimination is concerned. This finding is contrary to the recommendations of commercial biofilter manufacturers but shows that the process culture easily survives a significant period of carbonaceous pollutant starvation and that the organisms remain active. Even so, more subtle effects of intermittent conditions on the operating life of the packing still require clarification.

Influence of Gaseous Phase Oxygen Partial Pressure

When considering the optimization of biofiltration processes, identification of the rate limiting parameter is of prime importance. Theoretical analyses¹⁵ have emphasized that the gas phase interfacial resistance can generally be neglected and that possible limitations located in the biofilm are either of a diffusional or of a biochemical nature. In the present case, as diffusion of MEK and MIBK was shown not to be a limiting factor,^{6–8} the process must be limited either by the diffusion of oxygen or by a step in the biodegradative pathway for ketones. However, the fact that MEK and MIBK have markedly different maximum (molar) elimination capacities is evidence contrary to the occurrence of oxygen limitation. Even so, experi-

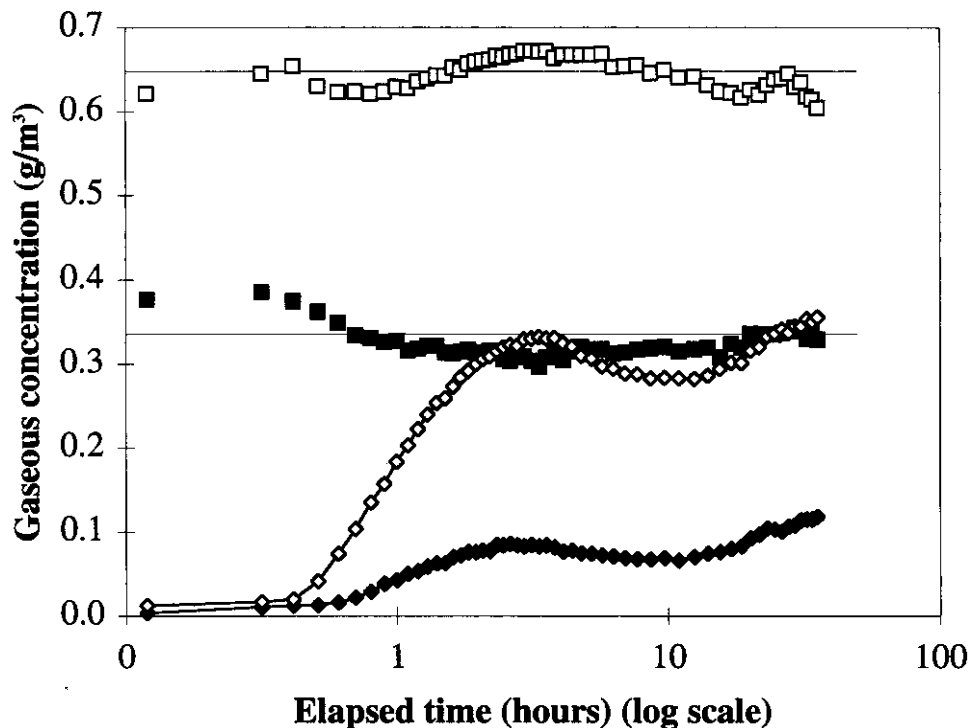


Figure 10. Biofilter startup after a 5-day starvation period. At time zero the inlet concentrations of MEK and MIBK were 0.34 and 0.65 g m⁻³, respectively. Air flow rate: 200 L h⁻¹ (volumetric loading: 44 m³ m⁻³ h⁻¹). MEK inlet (■) and outlet (◆); MIBK inlet (□) and outlet (◇).

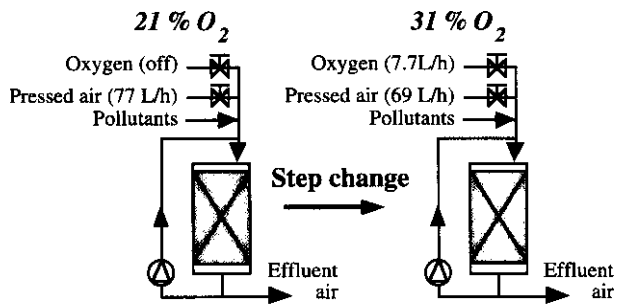


Figure 11. Experiment for a step change in oxygen partial pressure at constant pollutant concentrations for the study of possible oxygen limitation in the differential biofilter. Bed height 22 cm, total air flow rate 77 L h^{-1} , recycling flow rate 720 L h^{-1} .

ments were performed, as indicated schematically in Figure 11, in order to prove an absence of oxygen limitation. High pollutant concentrations and differential operating modes⁶ were chosen so that the eventuality of oxygen limitation could be investigated.

The results in Figure 12 indicate the time course for inlet and outlet concentrations during a 7-h switch from a low to a high oxygen content gas phase. Examination of Figure 12 shows a slight decrease in the MEK outlet concentration under high oxygen content operating conditions, but the numerical values reported in Table I show insignificant differences between the two oxygen supply situations. This confirms that oxygen limitation does not occur during MEK

and MIBK elimination in the biofilter systems studied. Similar experiments with conventional biofilters also lead to the same conclusion (unpublished results). As far as biofiltration in general is concerned, oxygen limitation is rarely reported. This is because the active biofilm is relatively thin and because of the low pollutant concentrations involved. However, the fact that acidic and other intermediates were formed in overloaded biofilters treating ethanol⁹ may be due to oxygen limitation. In bioscrubbers, where higher diffusional resistances and generally higher pollutant concentrations are involved, limitation by oxygen is much more likely to occur.

The absence of oxygen limitation emphasizes the fact that process optimization should involve the optimization of both biomass densities and specific pollutant biodegradative activities. However, this will only be possible after significant progress has been made both with respect to the physiology of immobilized microorganisms and after definition of the pollutant biodegradation kinetics applicable to biofilters.

CONCLUSIONS

Transient-state experiments in biofilters provide valuable information concerning the behavior of such systems under actual operating conditions. They also help in developing an understanding of pollutant removal and permit the establishment of a knowledge

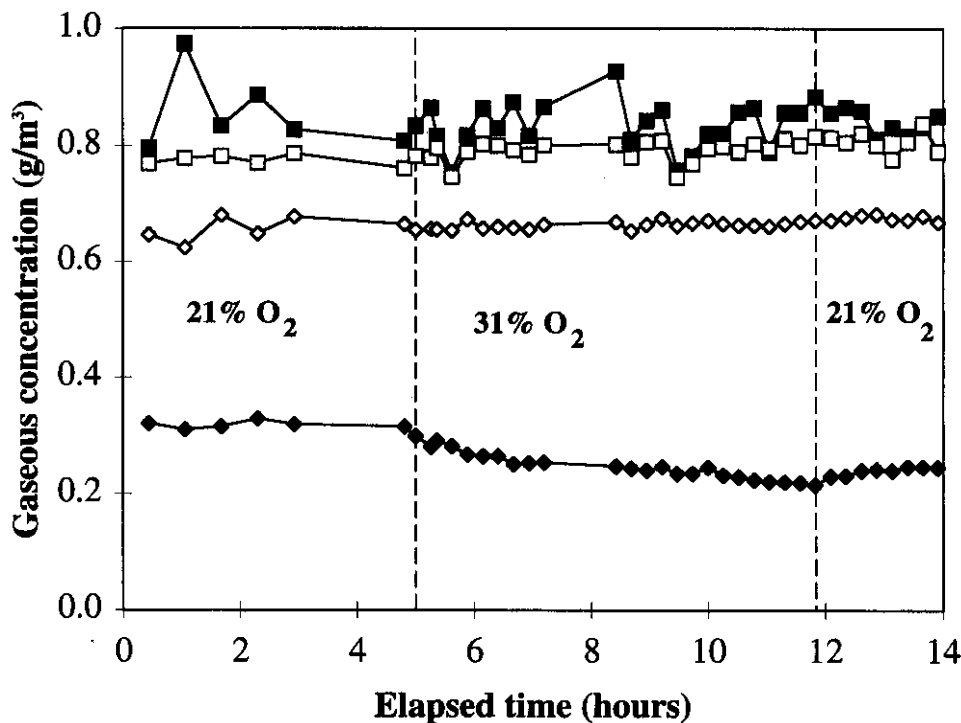


Figure 12. Influence of gas phase oxygen content on the removal of MEK and MIBK in the differential biofilter; total inlet flow 77 L h^{-1} . The vertical dashed lines represent the points of change from 21 to 31% oxygen, MEK inlet (■) and outlet (◆); MIBK inlet (□) and outlet (◇).

Table I. Stationary average (\pm error) for inlet and outlet concentrations and normalized elimination capacities before, during, and after the step change in gas phase oxygen content.

Parameter	Before step change, 21% O ₂	During step change, 31% O ₂	After step change, 21% O ₂
MEK inlet conc. (g m ⁻³)	0.84 \pm 0.03	0.83 \pm 0.02	0.83 \pm 0.01
MIBK inlet conc. (g m ⁻³)	0.77 \pm 0.01	0.79 \pm 0.01	0.80 \pm 0.02
MEK outlet conc. (g m ⁻³)	0.30 \pm 0.01	0.25 \pm 0.01	0.24 \pm 0.00
MIBK outlet conc. (g m ⁻³)	0.65 \pm 0.01	0.66 \pm 0.00	0.67 \pm 0.00
MEK degraded (g m ⁻³ h ⁻¹)	36.4 \pm 2.6	39.8 \pm 1.8	39.6 \pm 1.0
MIBK degraded (g m ⁻³ h ⁻¹)	8.1 \pm 1.3	8.7 \pm 0.7	8.7 \pm 1.5
Total degraded (g m ⁻³ h ⁻¹)	44.5 \pm 3.9	48.6 \pm 2.5	48.3 \pm 2.5

Note: No significant increase in process efficiency was observed.

base that is presently lacking in the literature. The initial startup time of the biofilter was shown to be short, with less than 5 days being required before complete removal of pollutant was achieved. Effective inoculation of the packing material favorably influences the startup. The lag phase for MIBK removal was shorter than that for MEK removal. During the acclimation phase, the elimination capacity increased exponentially. The doubling times for MEK and MIBK elimination capacities were 0.4 and 1.0 days, respectively.

Step changes both in pollutant concentration and flow rate demonstrated that the biofilter adapted rapidly to the new operating conditions. During transient-state operation, MEK/MIBK interactions and sorption/desorption processes were shown to play important roles. In most cases, about 2–5 h were generally needed after the step changes before a new steady state was established, a much shorter time than reported by Shareefdeen and Baltzis¹⁶ for toluene in a peat/perlite biofilter.

Pollutant pulses to biofilter reactors showed that when MEK was pulsed, both MEK and MIBK biodegradation rates were reduced in the upper part of the biofilter. This demonstrated that, under the extremely high concentrations of MEK involved, the MEK self-inhibited its biodegradation. The MEK pulses locally and persistently deactivated the process culture. Nevertheless, MEK was efficiently degraded in the bottom part of the biofilter where concentrations were noninhibitory. MIBK pulses had very little influence on the system, neither deactivation nor self-inhibition or MEK cross-inhibition was observed, most probably due to both the high Henry coefficient for MIBK and the inherent process biology.

Biofilters were shown to be capable of withstanding a 5-day period of complete starvation with immediate recovery to full performance when starvation ceased. However, the influence of starvation on the packing operating life was not investigated.

Step changes in oxygen partial pressure of the air stream, performed under high MEK and MIBK concentrations in the differential biofilter, demon-

strated the absence of oxygen limitation, which confirms that, as far as the optimization of biofiltration process is concerned, major attention should be directed toward the process biology rather than toward mass transfer effects.

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