Behavior of Biofilters for Waste Air Biotreatment. 1. Dynamic Model Development

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An novel diffusion reaction model for the determination of both the steady-state and transient-state behavior of biofilters for waste air biotreatment is developed and discussed. The model considers the reactor to comprise finite sections, for each of which transient mass balances are established and solved by digital simulation. The elimination of methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK) vapors from air as single and mixed pollutants serves as an example to illustrate and discuss both the model's response and its parametric sensitivity. Experimental evaluation of the model is presented in part 2 of this paper.

Introduction

Biological waste air treatment processes offer a cost-effective solution for the treatment of large volumetric airstreams containing low levels of pollutants. However, in spite of their widespread use in a broad spectrum of industries, such processes have only been subject to a minimum of modeling. Accordingly, empirical knowledge dictates the design and scale-up of biofiltration plants, even though substantial performance improvement could be expected from a more comprehensive knowledge of the individual processes involved in pollutant elimination. Because of the complexity of the several steps involved in pollutant elimination, biofilters are often considered as mysterious "black boxes" within which pollutants vanish as a result of the action of capricious microbes. Therefore, the development of appropriate models and their validation are required for improved process design and performance.

Biofilters are reactors in which a humid polluted airstream is passed through a porous packed bed on which pollutant-degrading microbial cultures are naturally immobilized. Biofilters excel in two main domains; in the removal of odoriferous compounds (1-4) and in the elimination of volatile organic chemicals (1, 4-10), primarily solvents, from waste air. Under optimum conditions, the pollutants are fully biodegraded without the formation of aqueous effluents.

In the present work, a new approach to biofilter modeling in response to the industrial need for more reliable information concerning not only steady state but also transient responses of biological filters is presented. Additionally, a major interest exists in the development of adequate models as a basis for the conceptual understanding of biofilter operation. The aerobic biodegradation of methyl ethyl ketone (MEK) and of methyl isobutyl ketone (MIBK) vapors in downward flow biofilters was selected as a model system. The study of binary pollutant elimination appeared to provide much greater scope for developing an understanding of biofiltration processes than did studies of single pollutant elimination (7, 11).

Previous investigations (9, 12, 13) involving biofilter modeling solved steady-state equations either analytically or numerically by iteration. Ottengraf *et al.* (9, 12) solved analytically the biolayer concentration profile and integrated it over the height of the biofilter to obtain the amount of pollutant biodegraded in the whole biofilter, assuming either first- or zero-order kinetics. The resulting solution was presented in terms of dimensionless groups. However, such an approach cannot be used to describe interactions between multiple substrates (7), transient states, or changes in the reaction order within the reactor.

Hirai *et al.* (3) correlated experimental results, considering the biofilter bed as a homogeneous plug-flow reactor with Michaelis–Menten type degradation kinetics. Neither diffusion nor phase transfer processes were taken into

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FIGURE 1. Stagewise model of biofilters showing the structure considered for finite-differencing. Biofilters are divided into ideally mixed subdivisions.

account. Such an approach may be useful for correlating sets of results but does not describe the fundamental steps involved and, therefore, cannot be applied over a wide range of operating conditions.

Shareefdeen *et al.* (13) developed a mathematical model for describing methanol biofiltration. This quasi-steadystate model based on the growth of biomass could not be used to describe short-term transient behavior. The model parameters were mostly determined in non-biofilter systems, and it was assumed that either methanol or oxygen was depleted in the biofilm. This may be the case for methanol but will not generally be true for other pollutants.

All the above models failed to explain dynamic phenomena and interactions between multiple pollutants during their elimination. The mathematical model developed herein has the advantages of describing both steadystate and dynamic behavior, even when pollutant interactions occur.

It should be recognized that there are numerous of models available for biofilm or biological trickling filter description (14-19). However, because of the absence of a free liquid phase in gas-phase biofilters, major differences in the nature of the biofilm (nonsubmersion) exist, and such models cannot be directly applied for the simulation of biofilter operation.

Model Development

The approach chosen is based on dynamic mass balances and uses the simulation techniques described by Dunn *et al.* (20) and Ingham *et al.* (21).

For modeling purposes, the biofilter height is divided into layers as shown in Figure 1. Within each layer three main sections are considered: the gas phase, the biofilm, and the liquid sorption volume. The sorption volume consists of water content dispersed within the carrier.



FIGURE 2. Schematic description of the model for one section of the column. The polluted airflows through the gaseous section, gas biofilm equilibrium is assumed, and simultaneous diffusion and biodegradation (symbolized by circular arrows) of the pollutants occurs in the biofilm subdivisions. No biodegradation of the pollutants occurs in the sorption volume.

Further, the biofilm is divided into four subdivisions, with each subdivision being considered to be ideally mixed. In the present model, the biofilter height was considered to comprise 10 layers, corresponding to the essentially plug-flow tracer response (*11*).

The fate of the pollutants in any section is illustrated in Figure 2 and can be described as follows. The polluted airflows downward so that convection is the vector of pollutant transport in the gaseous phase. At the gas—biofilm interface, equilibrium is assumed to occur, i.e., gaseous and interfacial liquid concentrations are related by Henry's law. In the biofilm, the pollutants simultaneously diffuse and are consumed by the microorganisms. Storage of the pollutants in the sorption volume is also possible, but only after their diffusion through the whole thickness of the biofilm. Figure 1 illustrates the overall structure considered for the mass balances, while Figure 2 illustrates modeling details for one section. The following assumptions were made:

1. Each subdivision, as defined in Figures 1 and 2, is ideally mixed.

2. The gas-phase interfacial resistance is negligible.

3. The gas and the liquid (biofilm) phases are in equilibrium at the interface.

4. The biofilm is treated as a planar surface.

5. Substrate transport between the liquid subdivisions (biofilm and sorption volumes) is by diffusion and can be described by an effective diffusion coefficient.

6. The mass transfer coefficient between the last biofilm subdivision (subdivision 4) and the sorption volume is the same as between adjacent biofilm subdivisions.

7. Oxygen limitation does not occur. This was confirmed experimentally by operating the biofilter at a high pollutant loading and switching to enhanced oxygen concentration (31%) in the waste air without significant changes in the elimination capacity (11). Mass balances for oxygen could be incorporated if deemed necessary.

8. The volume of the sorption volume is assumed to be equal to the water content of the support material minus the biofilm volume, and no biological reaction takes place within the sorption volume.

9. In the biofilm, no net growth of biomass is assumed so that kinetic constants remain constant over the time considered. Michaelis-Menten type kinetics with competition between substrates is assumed (22).

10. The biomass, i.e., the biocatalyst, is homogeneously distributed throughout the biofilm and can mediate the degradation of both substrates simultaneously.

The introduction of a liquid sorption volume proportional to the water content of the support material is supported by the fact that sorption of both ketones on the humid support material correlates reasonably well with their solubility in the liquid phase (11). No biological reaction is assumed in the sorption volume because of its dispersion throughout a matrix in which the pores are too small for microbial penetration (23). Accordingly, the matrix is assumed to have only a sponge function for water and pollutant storage. As defined, the sorption volume influences only transient-state behavior (11). It acts as a dynamic reservoir for pollutants and, therefore, buffers fluctuations in operating conditions.

Dynamic mass balances are written for both pollutants in each subdivision. In the following equations, *C* refers to gaseous concentrations and *S* to liquid concentrations.

Mass Balance over the Gas Phase. For the gas phase in the layer w, the dynamic balance for the gaseous concentration $C_{j,w}$ can be written as

$$\frac{V\epsilon}{W}\frac{\mathrm{d}C_{j,w}}{\mathrm{d}t} = G(C_{j,w-1} - C_{j,w}) - J_{j,w}\frac{AV}{W} \tag{1}$$

where $(V \in /W)$ is the volume of each gaseous subdivision, (AV/W) is its interfacial area, *G* is the total gas flow, *W* is the total number of layers, index *w* refers to the layer considered, where $1 \le w \le W$.

The diffusion flux J of component j into the biofilm is evaluated by finite differentiation:

$$J_{j,w} = D_j \left(\frac{\mathrm{d}S_{j,w}}{\mathrm{d}z}\right)_{z=0} = D_j \frac{S_{j,0,w} - S_{j,1,w}}{Z/N} \tag{2}$$

Gaseous concentrations $(C_{j,w})$, and interfacial concentrations $(S_{j,0,w})$ are linked by the interfacial equilibrium hypothesis:

$$S_{i,0,w} = C_{i,w}/H_i$$
 (3)

Mass Balances over the Biofilm. In the biofilm, the dynamic mass balance over a subdivision n is

$$\frac{AV}{W}\frac{Z}{N}\frac{\mathrm{d}S_{j,n,w}}{\mathrm{d}t} = D_{j}\frac{AV}{W}\left(\frac{S_{j,n-1,w} - S_{j,n,w}}{Z/N} - \frac{S_{j,n,w} - S_{j,n+1,w}}{Z/N}\right) - R_{\mathrm{s}_{j,n,w}}\frac{AV}{W}\frac{Z}{N}$$
(4)

where (AV/W)(Z/N) is the volume of one biofilm subdivision and (AV/W) is its cross section. R_{s_j} is the biodegradation rate, and N is the total number of biofilm subdivisions. Indices n and w refer to the number of biofilm subdivisions and biofilter stages, respectively. In eq 4, the term in parentheses associated with D represents the incoming and outgoing pollutant diffusion fluxes in the subdivision, as given by the finite-difference gradients.

Considering a nongrowing biofilm, the degradation rate R_{sj} is given for each subdivision in the biofilm by Michaelis– Menten type kinetics (22), with competition between the substrates when MEK and MIBK are biodegraded simultaneously. Hence

$$R_{s_{j,n,w}} = \frac{V_{m_j} S_{j,n,w}}{K_{m_j} (1 + I_{n,w} / K_i) + S_{j,n,w}}$$
(5)

where $I_{n,w}$ is the concentration of the competitive substrate, namely, MEK, when MIBK is considered and, conversely, MIBK when MEK is considered. K_i is the inhibition constant of I on the removal rate of j.

Other types of kinetics (22) such as noncompetitive (eq 6) or uncompetitive (eq 7) inhibition were evaluated, but the competitive inhibition kinetics (eq 5) gave the best results and was used for further modeling.

$$R_{\rm s} = \frac{V_{\rm m}S}{(1 + I/K_{\rm i})(K_{\rm m} + S)} \qquad \text{noncompetitive} \quad (6)$$

$$R_{\rm s} = \frac{V_{\rm m}S}{K_{\rm m} + S(1 + I/K_{\rm i})} \qquad \text{uncompetitive} \qquad (7)$$

Mass Balance over the Sorption Volume. In the sorption volume, where no biological reaction takes place and assuming the mass transfer coefficient is equal to that in the biofilm, it follows that

$$\frac{\text{TSV}}{W}\frac{\mathrm{d}S_{j,5,w}}{\mathrm{d}t} = D_j \frac{AV}{W} \left(\frac{S_{j,4,w} - S_{j,5,w}}{Z/N}\right) \tag{8}$$

As the total sorption volume (TSV) is assumed to be equal to the difference between the volume of water in the system and that of the biofilm

$$TSV = V(1 - \epsilon)mc - VAZ$$
(9)

where mc is the moisture content of the packing material.

System Solution. System equations are simplified with respect to substrate concentration, interfacial area, etc.,

TABLE 1 Model Parameters for Dynamic Simulation of Elimination of MEK and MIBK in Biofilters (11, 25)

biofilter characteristics			ymbol	value	ilue unit	source
interfacial area per volume unit biofilm thickness (sorption volu porosity of the filter bed	counted)	A Z €	150 100 0.5	m² m ^{−3} µm	adapted from ref 13 adapted from ref 13 mean residence time studies of pulses of inert cas in the biofilter bed (11)	
moisture content of the packing material			mc 60		wt %	drying of weighed packing samples (11)
pollutant characteristics	symbol	MEK	N	ЛІВК	unit	source
effective diffusion coefficient	D	2.85 × 10 ⁻¹⁰	5.37	× 10 ⁻¹⁰	m² s ⁻¹	model fitting of sorption experiments on inactive packing material (11)
maximum degradation rate	V_{m}	22.5×10^{-4}	5.51	× 10 ⁻⁴	kg m ⁻³ s ⁻¹	model fitting of independent single pollutant degradation experiments in biofilters (11)
Michaelis-Menten constant	K _m	1.37 × 10 ⁻³	1.49	× 10 ⁻³	kg m⁻³	model fitting of independent single pollutant degradation experiments in biofilters (11)
competition-inhibition constant	κ_{i}	3.70×10^{-4}	1.32	× 10 ⁻³	kg m⁻³	model fitting of independent mixed pollutant degradation experiments in biofilters (11)
Henry coefficient	Н	2.35×10^{-3}	5.71	× 10 ⁻³		direct GC measurements of gaseous and aqueous phase concentrations (11)

and are written in a form that is accepted by simulation language, namely:

for the gas phase

$$\frac{\mathrm{d}C_{j,w}}{\mathrm{d}t} = \frac{GW}{V\epsilon}(C_{j,w-1} - C_{j,w}) - D_j \frac{AN}{\epsilon Z} \left(\frac{C_{j,w}}{m_j} - S_{j,1,w}\right) \ (10)$$

for the biofilm

$$\frac{\mathrm{d}S_{j,n,w}}{\mathrm{d}t} = D_j \frac{N^2}{Z^2} (S_{j,n-1,w} - 2S_{j,n,w} + S_{j,n+1,w}) - R_{S_{j,n,w}} \tag{11}$$

where $R_{s_{j,n,w}}$ is given by eq 5

for the sorption volume

$$\frac{\mathrm{d}S_{j,5,w}}{\mathrm{d}t} = D_j \frac{AVN}{T\mathrm{SV} \times Z} (S_{j,4,w} - S_{j,5,w}) \quad (12)$$

where TSV is given by eq 9.

This system of equations was solved using the SimuSolv program (24), which is an interactive mathematical modeling tool for simulating physical systems defined by algebraic and differential equations. The program allows the optimization of model parameters by nonlinear curve-fitting of experimental data. The SimuSolv runs on mainframe or workstation platforms and employs the ACSL language.

From the different integration methods available, Gear's Stiff algorithm was chosen. This algorithm is of variable step length and of variable order and runs significantly faster than other Runge-Kutta or Runge-Kutta-Fehlberg methods. Depending on the model, the final integration time, and the maximum integration step, an extended CPU time was required.

To determine the model parameters, the system of equations was optimized to coincide with the results for a specific series of experiments (11, 25). The use of the SimuSolv program allowed both optimization of model parameters by nonlinear curve-fitting and estimation of the quality of the result obtained.

Results and Discussion

In the present study, the model is applied to the dynamic simulation of a realistic operating case and examined with

TABLE 2

Conditions for Dynamic Simulation of Simultaneous Elimination of MEK and MIBK in Biofilters

biofilter bed height biofilter bed area airflow rate changes in inlet concentrations	1 (m) 1 (m ²⁾ 45 (m ³ h ⁻¹⁾
hour 0 hour 10 hour 20	0.5 g m ⁻³ 2.0 g m ⁻³ 0 g m ⁻³
MIBK from hour 0 on, constant	0.5 g m ⁻³

respect to its parametric sensitivity for steady-state behavior. The values of the model parameters selected for each pollutant are listed in Table 1.

Dynamic Response. Here, a simulation is presented for a case where an active biofilter is restarted after a severalday interruption with the inlet concentration of one pollutant, MIBK, kept constant and the concentration of the other pollutant, MEK, increased in a stepwise manner and subsequently disconnected. The simulation was based on the model parameters listed in Table 1 and the conditions listed in Table 2.

In Figure 3, both the inlet concentration and the computed dynamic response of the biofilter to the situated conditions described above are shown. The biofilter evolution concentration profiles with respect to time are given in Figure 4.

As seen in Figures 3 and 4, a predicted steady state is reached after 3 h, after which time complete removal of MEK and 80% removal of MIBK are predicted. After the restart, the dynamic increase of pollutant penetration and the marked effect on concentration profiles of competition between MEK and MIBK can be seen in Figure 4 after 0.5, 1, and 6 h, respectively.

After 10 h, the MEK inlet concentration was increased stepwise. Whereas the model predicts a breakthrough of MEK, 95% of the MEK was removed. Significant repression of MIBK degradation was predicted, resulting in an increase in the MIBK outlet concentration from 0.1 to 0.4 g m⁻³. Corresponding modifications in the concentration profiles are shown in Figure 4 after 11 and 18 h, respectively.



FIGURE 3. Dynamic simulation of the simultaneous removal of MEK and MIBK vapors from a waste airstream in a biofilter. In the upper graph, step changes in inlet concentrations are shown. In the lower graph, the dynamic response predicted by the biofilter model is shown. The vertical dashed lines indicate the times chosen for the evaluation of the biofilter concentration profiles reported in Figure 4.

In the simulated case, MEK was interrupted after 20 h. However, persistence of MEK in the outlet stream for as long as 2 h after interruption was predicted as a direct consequence of a combination of desorption and biodegradation. Thereafter, MIBK was removed as a single pollutant, undergoing complete elimination, contrary to the first 10-h phase where its breakthrough was induced by the inhibition of MEK. Significant differences could be observed in the MIBK concentration profile after 24 h compared with after 6 h. This illustrates the major impact of competing pollutants on each other and emphasizes the necessity of determining and validating appropriate kinetics for multiple pollutants elimination.

Detailed examination of concentration and of reaction rate (11) profiles in the biofilter reveal that axial gradients lead to changes in reaction rate order, which varied both as a result of operating conditions and of the position in the reactor. When individual pollutants are removed, zeroorder kinetics are usually observed at the inlet of the reactor, but as a result of pollutant depletion, these changed to essentially first-order kinetics in the column. With multiple pollutants, complex changes in the order of the reaction rate occurs, depending on both the kinetics and the operating conditions. Such changes justify the use of essentially unsimplified, complex biodegradation kinetics in the model. As a result, the model displays necessary flexibility for describing various operating conditions for any pollutant within a broad range of physicochemical properties and biodegradation rates.

Parametric Sensitivity of the Model. The parametric sensitivity of the model was analyzed for MEK removal as a single pollutant on the basis of the conditions listed in Table 3. This analysis permits determination of the relative importance of each parameter involved in the biofiltration process.

Two different inlet concentrations of the pollutant were considered in order to investigate the general trends with respect to parametric sensitivity. Therefore, two sets of results are given, one for a low inlet concentration (A) and the other at a high inlet concentration (B). Additionally, variations in the inlet pollutant concentrations, airflow rates, and bed height provided valuable information on the performance of the biofilter system under an extended range of operating conditions.

As the biofilter considered is 1 m in height and 1 m² in surface area, the airflow rate is equal to both the surface and the volumetric loadings. If not otherwise stated, results are given as contour plots for the elimination capacity (in g m⁻³ h⁻¹), as defined in eq 13 with respect to the two parameters varied and indicated on the axes. Under the conditions chosen, complete removal of MEK corresponds to 50 and 150 g m³ h⁻¹ for inlet concentrations of 1 and 3 g m⁻³, respectively. The pair of parameters determined by simulation of the experimental results is indicated in the



FIGURE 4. Evolution of concentration profiles in the biofilter with respect to time for simultaneous removal of MEK and MIBK corresponding to Figure 3. The symbols (MEK **m**, MIBK **D**) are the modeled local gaseous concentrations in the different sublayers of the model. Because of the down-flow mode of operation, the highest local solvent concentrations occurred at a relative bed height of 1 (inlet), and the lowest occurred at a relative height of 0 (outlet). Times correspond to the vertical dashed lines shown in Figure 3.

TABLE 3 Conditions for Study of Parametric Sensitivity of Model for MEK and MIBK Elimination in Biofilters

biofilter bed height	1 m
biofilter bed area	1 m ²
airflow rate	50 m ³ h ⁻¹
MEK inlet concentration	1 and 3 g m ⁻³
MEK and MIBK inlet concentrations	
mixtures of MEK and MIBK: each	0.7 g m ⁻³

figures as a black dot. The parameters maintained constant have their values listed in Table 1.

elimination capacity =

$$\frac{\text{(inlet - outlet concentration)} \times \text{airflow}}{\text{biofilter bed volume}}$$

$$(g \text{ m}^{-3} \text{ h}^{-1}) (13)$$

The influence of the effective diffusion coefficient D and of the maximum degradation rate $V_{\rm m}$ are of particular interest as generally one of these parameters dictates the elimination rate. In Figure 5, a domain where MEK diffusion control occurs at low diffusion coefficients is shown on the left-hand side of each figure. In this operating domain, the maximum biodegradation rate exceeds the maximum diffusion rate, and the pollutant is degraded before penetrating into the deeper subdivisions of the biofilm and into the sorption volume. On the other hand, when $V_{\rm m}$ is low, the process is obviously controlled by the biodegradation rate and the biofilm gradients are negligible. This is most noticeable at high gaseous phase pollutant concentrations (Figure 5B for $D > 1 \ 10^{-10} \ m^{-2} \ s^{-1}$), where a linear increase in elimination capacity from 10 to 140 g m⁻³ h⁻¹ is observed. The increase in inlet pollutant concentration from 1 to 3 g m⁻³ enlarges the domain where the process is limited by the biodegradation rate, whereas the diffusionlimited domain is essentially unaffected by the pollutant concentration. The border between the diffusion and reaction controlled regimes depends on both the diffusion and the reaction rates as well as on the interfacial concentration. This can be best explained by considering the influence of D and V_m on the concentration profile in the biofilm, particularly on the conditions necessary for complete pollutant depletion within the biofilm.

The modeled values for $V_{\rm m}$ and D, indicated by the black dot in the figures, show that case A is essentially unlimited, i.e., complete elimination is achieved, and that case B is clearly limited by the biodegradation rate.

The sensitivity of MEK elimination to the Michaelis– Menten constant, K_m , with respect to the maximum degradation rate is depicted in Figure 6. Small changes in K_m generally do not lead to major effects as can be seen in Figure 6, where the maximum degradation rate is again found to be the most sensitive parameter. However, when major changes in K_m are made, significant effects on process efficiency are observed. Therefore, K_m cannot be neglected in the description of the biodegradation kinetics. Examination of the effect of concentration increases in Figure 6 shows that, contrary to what should be expected from the expression for reaction rates, the influence of K_m is



FIGURE 5. Parametric sensitivity of the MEK elimination capacity reported in g m⁻³ h⁻¹ with respect to the effective diffusion coefficient and the maximum degradation rate. MEK inlet concentration is (A) 1 g m⁻³; (B) 3 g m⁻³.



FIGURE 6. Parametric sensitivity of the MEK elimination capacity with respect to the maximum degradation rate V_m and to the Michaelis-Menten constant K_m . MEK inlet concentration is (A) 1 g m⁻³; (B) 3 g m⁻³.

undiminished when the pollutant concentration increases. This is of particular importance during the removal of pollutant mixtures, when the apparent K_m is markedly increased by competition (see eq 5) with a subsequent reduction of the degradation rates of individual pollutants.

The Henry coefficient is one of the most important physicochemical properties of the pollutant as far as biofiltration is concerned. In Figure 7, the sensitivity of the biofilter model to the Henry coefficient is analyzed with respect to the maximum degradation rate. The Henry coefficient is varied from 10^{-3} (low volatility component, i.e., high interfacial equilibrium concentration) to 0.1 (highly volatile component, i.e., low interfacial equilibrium concentration), corresponding to a realistic range of partition coefficients (i.e., 1/H) of 1000:10.

Examination of Figure 7 shows that the Henry coefficient sensitivity remains moderate as long as the $V_{\rm m}$ rate is low, i.e., in the reaction rate controlled domain. However, at $V_{\rm m}$ values greater than 0.003 kg m⁻³ s⁻¹, the impact of the Henry coefficient on the overall elimination capacity becomes predominant. This can be explained by the increasing role of diffusion when degradation rates rise and, hence, the increasing importance for high liquid equilibrium concentrations (i.e., low H values) to ensure

film penetration and significant degradation rates.

Figures 8 and 9 are not strictly parametric sensitivity studies but present further illustration of biofilter performance under various operating conditions. The influence of bed height and MEK inlet concentration on both elimination capacity and percentage removal, as defined in eq 14, is shown in Figure 8, panels A and B, respectively. One clearly sees an increase in elimination capacity parallel to the increase in inlet pollutant concentration and a corresponding decrease in percentage removal when the increase is outside the domain of complete removal.

$$removal = \frac{inlet - outlet concentration}{inlet concentration} \times 100$$
 (%) (14)

Similarly, elimination capacity and removal are reported with respect to airflow rate and inlet concentration in Figure 9.

Figures such as Figures 8 and 9 are extremely useful for design purposes as they clearly show performance at any operating conditions, thereby permitting optimization either of the elimination capacity or of the percentage removal.



FIGURE 7. Parametric sensitivity of MEK elimination capacity with respect to the Henry coefficient and to the maximum degradation rate. MEK inlet concentration is (A) 1 g m⁻³; (B) 3 g m⁻³.



FIGURE 8. Biofilter performances for MEK removal at a given airflow rate of 50 m³ h⁻¹, with respect to both biofilter bed height and MEK inlet concentration. Reported are (A) the elimination capacity in g m⁻³ h⁻¹ and (B) the percentage removal. The dotted vertical lines represent the bed height chosen for this investigation.



FIGURE 9. Biofilter performances for MEK removal as a function of the airflow rate and the MEK inlet concentration for a constant bed height of 1 m. Reported are (A) the elimination capacity and (B) the percentage removal. The dotted vertical lines represent the airflow rate chosen for this investigation.

The parametric sensitivity of the model in the case of multiple pollutants is a complex problem because of the dependency of the biodegradation of the pollutants on each other (6, 7, 26). This is illustrated in Figure 10 where the gaseous phase concentrations are set at 0.7 g m⁻³ of MEK and 0.7 g m⁻³ of MIBK and the operating conditions are as



FIGURE 10. Parametric sensitivity of MEK (A) and MIBK (B) elimination capacities in g m⁻³ h⁻¹ with respect to both competitive inhibition constants. MEK and MIBK inlet concentration are both 0.7 g m⁻³, and operating conditions are as before. In the inset models, the concentration profiles of MEK both with and without MIBK for the present operating conditions are shown, and the increase in MEK penetration caused by the presence of MIBK is shown, although overall complete removal is observed in both cases.



FIGURE 11. Biofilter performance for simultaneous MEK (A) and MIBK (B) elimination in g m⁻³ h⁻¹ of each pollutant, resulting from different inlet concentrations of MEK and MIBK. Volumetric loading is maintained constant at 50 m³ m⁻³ h⁻¹.

indicated above. Under these conditions, complete removal of one pollutant represents an elimination of 35 g $m^{-3}\ h^{-1}.$

The results for the variation of the inhibition constants and their influence on the elimination capacity of MEK (A) and MIBK (B) are shown in Figure 10. It is obvious from Figure 10A that when $K_{i_{\text{MIBK on MEK}}}$ is lower than 0.001 kg m⁻³, a breakthrough in MEK results from the presence of MIBK, and increasing repression of MEK biodegradation by MIBK, parallel to the decrease in the inhibition constant, is observed. However, small changes in $K_{i_{MIBK on MEK}}$ around the value reported in Table 1, indicated by the black dot in Figure 10, do not lead to obvious diminution of the overall elimination capacity as complete removal of MEK is achieved. The inset graph in Figure 10A shows that for these values of K_i , even if complete removal of MEK is predicted, when mixed with MIBK, the MEK penetration profile in the biofilter column is greatly affected by the presence of MIBK. Therefore, if the parametric sensitivity to K_i would have been represented at partial removal of MEK, a much higher sensitivity of MEK elimination to $K_{i_{MEK}}$ on MEK would have been evident.

Examination of Figure 10B shows that MIBK biodegradation depends not only on the inhibitory effects of MEK but also on its own inhibitory effects on MEK biodegradation. This is clearly a consequence of the high sensitivity of MIBK biodegradation to the local concentration of MEK. Changes in $K_{i_{MIBK}}$ on MEK affect MEK concentration profiles and consequently the inhibitory effect of MEK on MIBK. Further, Figure 10 shows that when K_i values are increased substantially, inhibition decreases and, ultimately, the elimination capacity reaches values for the degradation of the individual pollutants, such that the pollutants are degraded essentially independently of each other.

The performance of a biofilter exposed to mixtures of MEK and MIBK is shown in Figure 11, where MEK elimination is significant over the whole spectrum of conditions but with a marked influence resulting from the presence of MIBK at the highest concentrations considered also being evident. MIBK inhibition is clearly quantified in panel B, where MIBK elimination is increasingly inhibited by increasing concentrations of MEK. MIBK elimination is shown to be independent of its own inlet concentration for low concentrations of MEK. As established elsewhere (11), this is because of the apparent "zero-order" kinetics, i.e., constant elimination capacity of a biofilter over a certain concentration or loading of pollutant, for MIBK removal in excess of a critical loading of approximately 25 g m⁻³ h⁻¹, i.e., 0.5 g m⁻³ inlet concentration of MIBK.

Conclusions

A novel model for the description of gaseous waste biofiltration has been developed and discussed. The model considered the biofilter height to be divided into 10 layers. Three main sections were considered in each layer: the gas phase; the biofilm, which was split into four subdivisions; and a reaction-free liquid sorption volume, which was directly proportional to the water content of the biofilter packing material. Michaelis-Menten biodegradation kinetics were assumed to apply in the biofilm, and competitive inhibition was included for cases involving the simultaneous degradation of pollutants. Simulation techniques were used to solve the dynamic mass balances. The biofilter model permitted a detailed description of local gas and biofilm concentrations during both steady- and transient-state biofilter operation. The simultaneous biodegradation of MEK and MIBK served as a test system for discussion of both the dynamic and steady-state biofilter operation and of the parametric sensitivities of the model. The experimental evaluation of the model is presented subsequently (26).

Simulation of a realistic case emphasized the dynamic response of the biofilter to step changes in the operating variables and identified the consequences of competition between the pollutants undergoing treatment. The dynamic evolution of concentration profiles in the biofilter allowed one to distinguish between the several kinetic regimes that occurred under various operating conditions.

The analysis of the parametric sensitivity of the model developed herein exhibited interesting features for single and mixed pollutant removal in biofilters. The biodegradation of MEK and of mixtures of MEK and MIBK was shown to be subject to overall limitation by the biodegradation rate, and the domains for probable diffusion limitation were defined.

The influence of K_m increased with increases in pollutant concentration, contrary to established interpretation of saturation kinetics which predicts a minor influence of K_m at high pollutant concentrations. Therefore, the K_m term can be expected to play a major role during the removal of multiple pollutants that exhibit competition kinetics, because it is multiplied by the inhibition term. Variations in the value of the Henry's law coefficient confirmed that, because of their favorable gas—biofilm equilibrium, pollutants with the lowest Henry coefficients are the easiest to remove from waste air, provided of course that they are biodegradable.

The sensitivity analyses of MEK and MIBK elimination in the case of multiple pollutant removal proved that MEK was less sensitive than MIBK to the presence of the other pollutant. This is because of the intrinsic properties of the microbes responsible for MEK and MIBK biodegradation and of the higher biofilm concentrations of MEK, which results from its lower Henry coefficient.

Furthermore, the characteristics of biofilters for the removal of MEK and MIBK mixtures were established by the model, providing quantitative information on the elimination of each ketone over a broad range of mixture compositions. Such information is of evident interest for design purposes.

Because of the versatility of the model illustrated here, the conclusions obtained in the present study can be extrapolated for other biofilter systems used for waste air purification. Additionally, the essentially simple model structure makes for easy adaptation for various situations and can even be modified to account for conditions such as oxygen limitation and byproduct inhibition.

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Nomenclature

 C_i (kg m⁻³) gaseous concentration of component j

- D_j (m² s⁻¹) effective diffusion coefficient of component j
- G (m³ s⁻¹) airflow rate
- H_i Henry coefficient of component j
- *I* component *I*, inhibitor in biodegradation kinetics *j* component *j*
- J_j (kg m⁻² s⁻¹) diffusion flux of component *j* into the biofilm
- $K_{i_{j \text{ on } t}}$ (kg m⁻³) competition inhibition constant of component j on component t
- K_{m_j} kg (m⁻³) Michaelis–Menten constant of component j

mc biofilter packing moisture content (in wt %)

- MEK methyl ethyl ketone
- MIBK methyl isobutyl ketone
- N number of biofilm subdivisions in each layer (here N = 4)
- *n* biofilm and sorption volume subdivisions $(1 \le n \le N+1)$

$$R_{s_i}$$
 (kg m⁻³ s⁻¹) degradation rate of component j

 $S_{j,n,w}$ (kg m⁻³) liquid concentration of component *j*, subdivision *n*, layer *w*

TSV (m³) total sorption volume

 $V_{\rm m}$ (kg m⁻³ s⁻¹) maximum degradation rate

- V (m³) total reactor volume
- W number of layer subdivisions (here W = 10)
- *w* biofilter layer subdivisions: $1 \le w \le W$
- Z (m, μ m) biofilm thickness (sorption volume not counted)
- z biofilm depth coordinate

Greek Symbols

 ϵ porosity of the filter bed

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