

The removal of volatile ketone mixtures from air in biofilters

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Abstract. The work reported concerns the removal of mixtures of two ketones, methyl ethyl ketone (*MEK*) and methyl isobutyl ketone (*MIBK*), which find wide application as industrial solvents, from effluent air streams in downward flow biofilters operating at relative humidities in excess of 95 percent. The inlet concentrations of the two pollutants were 300 mg m^{-3} *MEK* and 330 mg m^{-3} *MIBK*. Maximum elimination capacities achieved were $50 \text{ g m}^{-3} \text{ h}^{-1}$ for *MEK* and $20 \text{ g m}^{-3} \text{ h}^{-1}$ for *MIBK*. Marked interaction between the elimination of the two ketones was observed and established bio-physical models for the kinetic analysis of biofilter operation proved inadequate as far as the complex processes involved in multi-component biodegradable vapour elimination were concerned. The complexity of such systems requires further definition and the development of appropriate models for process evaluation and design.

List of symbols

a	$\text{m}^2 \text{m}^{-3}$	interfacial area per volume unit
C_g	mg m^{-3}	gaseous concentration
D_e	$\text{m}^2 \text{s}^{-1}$	effective diffusion coefficient
h, H	m	height, total bed height
K_1	s^{-1}	first order reaction rate constant
K_0	$\text{g m}^{-3} \text{s}^{-1}$	zero-order reaction rate constant
m_i	—	distribution coefficient of component i
U_g	m s^{-1}	superficial gas flow rate
δ	m	biolayer thickness
η	— or %	degree of conversion, removal ($\eta = (C_{gi} - C_{go})/C_{gi}$)

Subscripts

i	inlet
o	outlet
bf	biofilter

Definitions

<i>MEK</i>	methyl ethyl ketone
<i>MIBK</i>	methyl isobutyl ketone
Solvent load:	$\text{mg}_{\text{solvent}}/(\text{m}^3_{\text{biofilter}} \text{hour})$
Surface load:	$\text{m}^3_{\text{gas}}/(\text{m}^3_{\text{biofilter}} \text{hour})$
Volume load:	$\text{m}^3_{\text{gas}}/(\text{m}^3_{\text{biofilter}} \text{hour})$

1 Introduction

Throughout the present century, biotreatment processes have found increasingly widespread application for the

treatment of wastewater and waste aqueous slurry streams. Much more recently, biotreatment processes for waste gas streams [1] and for the remediation of grossly polluted environmental compartments [2] have also been proposed. In spite of the fact that waste streams are generally distinguished on the basis of their physical state, the biodegradation of the pollutants that they contain depends on series of essentially common microbially mediated process steps from either one or several of the elemental (biogeochemical) cycle(s) governing material transformation.

Biotreaters for waste gas streams are divided into two primary types; biofilters, which operate without a distinct free liquid phase and bioscrubbers, which operate with a free liquid phase. In biofilters, the relative humidity of the gas phase usually exceeds 95 percent, an operating condition under which surfaces will have significant quantities of water associated with them and which suggests that both biofilters and bioscrubbers function as biosorbers. This premiss is also supported by the failure of biofilters to achieve significant conversions [3] of slightly water soluble pollutants such as methane during single pass operation through a biofilter containing a methanotrophic consortium [4], whereas biofilters containing appropriate process cultures achieve complete conversion of significantly water soluble vapours [5, 6].

Both methyl ethyl ketone (*MEK*) and methyl isobutyl ketone (*MIBK*) are widely used industrial chemicals with annual productions exceeding 600,000 and 250,000 tonnes, respectively. The use of both chemicals as solvents results in their presence in both concentrated and dilute waste streams, frequently as mixtures. Whilst recovery and recycle is a realistic option for the former streams, economic considerations dictate that dilute, particularly dilute gaseous waste streams, are best subject to treatment, particularly when appropriate treatment process efficacies and costs can be achieved.

Provided equivalent performance can be obtained with similarly sized biofilters and bioscrubbers, both the simpler construction and the less complicated operation of the former will favour their selection for waste gas biotreatment. However, a critical operating factor pertain-

ing to system selection is sustainable operability. Whereas bioscrubbers function in an analogous manner to other submerged culture type bioreactors where sustainable performance is proven, biofilters require process cultures to function effectively under conditions where they are apparently in direct contact with the pollutant containing gaseous phase. It should also be mentioned that biofilters are unsuitable for the biotreatment of waste gas streams containing biodegradable chlorine and sulphur compounds, because of acid formation and the employment of bioscrubbers, with pH control, for such streams, is recommended.

In order to evaluate biofilter performance, biofilters enriched for process cultures that aerobically biodegrade *MEK* and *MIBK* have been selected for the present study. Both *MEK* and *MIBK* are significantly soluble in water (290 kg m^{-3} and 19 kg m^{-3} at 20°C , respectively) and Bridié et al. [7] have reported that in aerobic biodegradability tests, the two chemicals exhibit biochemical oxygen demands that are 83 and 76 percent of the theoretical oxygen demand, respectively, indicating that both chemicals are readily biodegradable under aerobic conditions.

2 Material and methods

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

2.1 Pollutant containing humid air stream

Compressed oil-free air is saturated with water vapour by sparging the air into a 50 dm^3 bottle containing deionized water and thermostated at 28°C . Two smaller compressed air streams were sparged into 0.5 dm^3 bottles containing either *MEK* or *MIBK* as required and subsequently mixed with the major humidified air stream. A metered flow of pollutant containing humid air stream was passed downwards through each of five vertical packed column biofilters operating under a range of selected parameters.

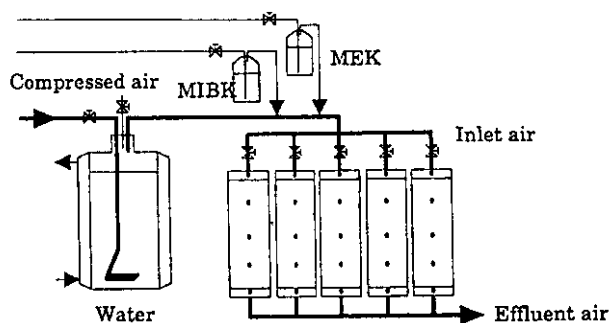


Fig. 1. Schematic diagram of the experimental system

Pollutant concentrations in the air streams were 300 mg m^{-3} of *MEK* and 330 mg m^{-3} of *MIBK* giving a total solvent concentration of 630 mg m^{-3} .

2.2 Biofilters and packing material

The biofilters were constructed from Plexiglas tubing and were 1 m in length and 80 mm in internal diameter. The upper and lower 80 mm of each column was packed with expanded clay spheres and the remaining 840 mm with Bioton, a commercially available biofilter packing (Clair-Tech, Utrecht, NL), comprising an equivolume mixture of compost and polystyrene spheres. Acid neutralising components are also added to the biofilter material. The voidage of the packing material, determined by studying the residence time distribution after a pulse of inert gas, was 51 percent. Before use, the packing material was inoculated with a concentrated enrichment culture. Sample ports were located at 0, 33, 59, 86 and 100 percent of the active packing height in each column. Column temperatures were maintained between 21° and 25°C . The gas flow rate through each individual biofilter was measured with a rotameter.

2.3 Inoculum

Solvent degrading enrichment cultures were grown on *MEK* and *MIBK* in shake flasks, with regular transfers, over a period of six months. The inoculum was prepared by concentrating 3 dm^3 of enrichment culture to 0.02 dm^3 by centrifugation. This was sufficient to coat 1 kg of packing material prior to its introduction into the columns.

2.4 Operating conditions

The active bed volume was 4.2 dm^3 and the mass of damp support material, comprising 60 percent water, was 0.95 kg per filter. Downward gas flow rates of 0.15 to $0.47 \text{ m}^3 \text{ h}^{-1}$ per biofilter were used, giving a surface loading of 30 to 95 m h^{-1} and a volumetric loading of 35 to 115 h^{-1} . The gas had a relative humidity greater than 95 percent and the pressure drop over the filter was less than 50 mm water gauge. Between each set of measurements the biofilters were allowed to stabilise for more than 4 days, after which time no changes in pollutant removal characteristics could be observed.

2.5 Analysis

The concentrations of *MEK* and *MIBK*, in gas phase samples were determined by gas chromatography. 1 ml gas samples were introduced into a Carlo Erba (Milan, I) type HRGC 5160 gas chromatograph fitted with a SE 54 column and operated isothermally at 70°C . The carrier

gas used was $1.83 \text{ dm}^3 \text{ h}^{-1}$ hydrogen and detection was with a flame ionisation detector. The detection limit was ca. 10 mg solvent per m^3 of gas.

3 Results

The first objective of the experimental programme was to determine the effects of mean effective gas residence time and of solvent loading, expressed as g solvent per m^3 biofilter volume and hour, on biofilter performance. The results, based on both outlet and mid point concentrations, are shown in Figs. 2 and 3, respectively, and it is clear that *MEK* was more rapidly biodegraded than was *MIBK*. Fig. 2 indicates that no *MEK* was detected in the treated gas stream at residence times greater than 16 seconds, whilst *MIBK* reached undetectable concentrations in the treated gas stream only at residence times greater than ca. 50 seconds. Even at a residence time as low as 8 seconds, 67 percent of the *MEK* was eliminated. In Fig. 3, the solvent degraded is plotted against the

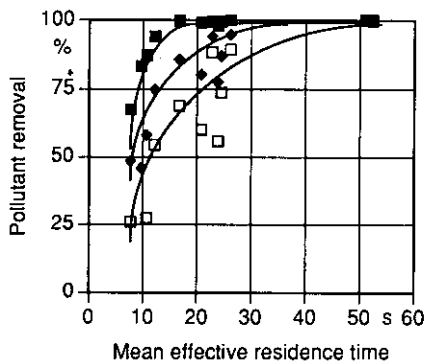


Fig. 2. Pollutant removal of *MEK* (■), *MIBK* (□), and total removal (◆) with respect to mean effective gas residence time in the system

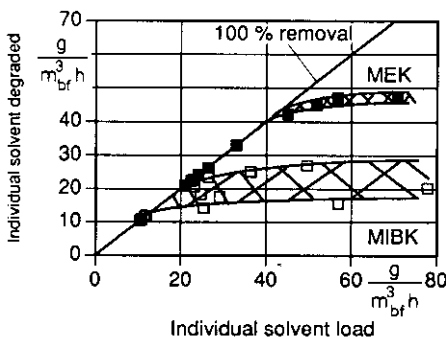


Fig. 3. Amount of *MEK* (■) or *MIBK* (□) biodegraded expressed in $\text{g m}^{-3} \text{ bf h}^{-1}$ with respect to the individual solvent load. The line (slope = 1) corresponds to total conversion of each substrate

corresponding solvent loading and it is clear that *MIBK* broke through the biofilter at a much lower solvent loading than did *MEK*. Neither detection of *MEK* nor of *MIBK* occurred at total solvent loadings of less than $20 \text{ g m}^{-3} \text{ h}^{-1}$, but above this loading significant break-through of *MIBK* was observed. However, break-through of *MEK* was not detected until total solvent loading exceeded $70 \text{ g m}^{-3} \text{ h}^{-1}$. At total solvent loadings above $70 \text{ g m}^{-3} \text{ h}^{-1}$, the amount of *MEK* degraded increased to an upper degradation limit at ca. $50 \text{ g m}^{-3} \text{ h}^{-1}$ but, of course, at these total loadings elimination was incomplete. The corresponding upper degradation limit for *MIBK* was ca. $20 \text{ g m}^{-3} \text{ h}^{-1}$.

A second objective was to obtain detailed information concerning the *MEK* and *MIBK* profiles in the biofilters during solvent elimination from the polluted air stream. Because of the down flow mode of operation, the highest local solvent concentrations occur at a relative bed height of 1 and lowest local solvent concentrations at a relative bed height of 0. The local concentration profiles for both *MEK* and *MIBK* when the polluted air stream flow was $0.342 \text{ m}^3 \text{ h}^{-1}$ are shown in Fig. 4. Although the removal patterns for the two solvents are markedly different, it is clear that simultaneous elimination occurred, but that the rate of elimination for *MEK* from the polluted air stream exceeded the corresponding rate of elimination for *MIBK*. Previous studies [8] had already shown that the presence of *MEK* in an air stream polluted with *MIBK* adversely affected both the removal capacity and the elimination rate of *MIBK* in a biofilter that had been prepared for *MIBK* removal.

The results shown in Figs. 5 to 7 provide local concentration data for *MEK*, *MIBK* and total solvent for polluted air flow rates of 0.149, 0.298, 0.342 and $0.468 \text{ m}^3 \text{ h}^{-1}$, respectively. With increasing air flow rate, the penetration concentration profile increased for each solvent. In the case of *MEK*, the profiles at different air flow rates were

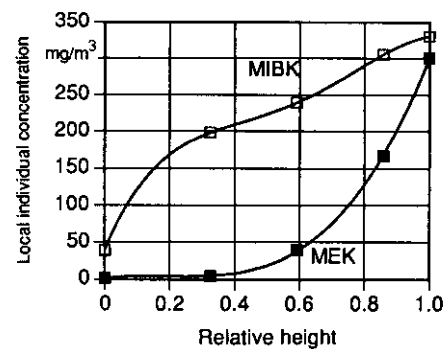


Fig. 4. *MEK* (■) and *MIBK* (□) concentration profiles as a function of the relative sampling height. The polluted air flow ($0.342 \text{ m}^3 \text{ h}^{-1}$) corresponds a total effective residence time of 23 seconds

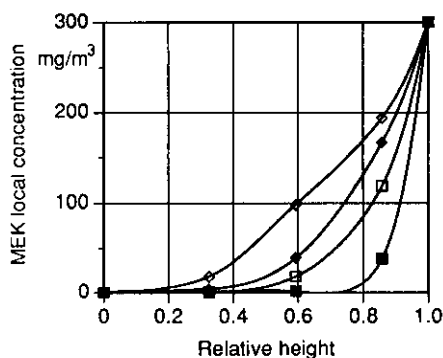


Fig. 5. MEK concentration profiles as a function of the relative sampling height. Polluted air flow: $0.149 \text{ m}^3 \text{ h}^{-1}$ (■), $0.298 \text{ m}^3 \text{ h}^{-1}$ (□), $0.342 \text{ m}^3 \text{ h}^{-1}$ (◆), $0.468 \text{ m}^3 \text{ h}^{-1}$ (◇)

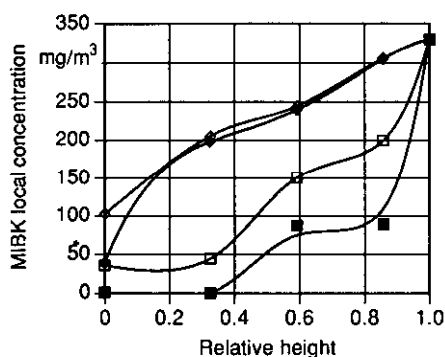


Fig. 6. MIBK concentration profiles as a function of the relative sampling height. Symbols as in Figure 5

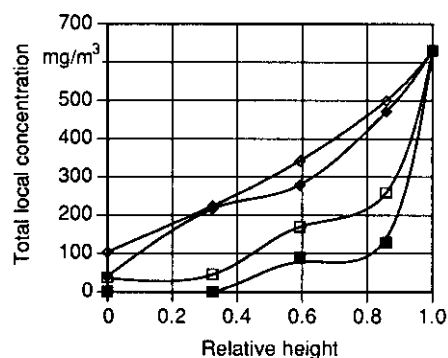


Fig. 7. Total solvent concentration profiles as a function of the relative sampling height. Symbols as in Figure 5

similar and, even at the highest flow rate used, elimination was complete. However the profiles for MIBK elimination were irregular and removal was incomplete at all but the lowest flow rate, in spite of the fact that with a similar

biofilter operating at much higher air flow rates, but similar concentrations of MIBK as a single pollutant, complete elimination occurred, indicating significant interactions between the respective elimination processes during simultaneous elimination. Examination of Fig. 7 indicates that the total solvents profile at a polluted air flow rate of $0.468 \text{ m}^3 \text{ h}^{-1}$ is virtually linear ($r = 0.98$), whilst at a polluted air flow rate of $0.149 \text{ m}^3 \text{ h}^{-1}$ the profile assumes an exponential form, suggesting that the rate determining step in the elimination process changes with respect to gas phase residence times in the biofilter.

4 Discussion

In order to develop a fundamental understanding of volatile mixed solvent elimination in downward flow biofilters, it is important to understand both individual component and overall elimination kinetics. A biophysical model that describes steady state elimination of individual carbon energy substrates has been proposed by Ottengraf [9]. The model is based on the following assumptions:

- 1) The gas phase interfacial resistance is negligible;
- 2) the gas phase is in plug flow;
- 3) nutrient transport in the biofilm is by diffusion and can be described by an effective diffusion coefficient, D_e ;
- 4) the biofilm thickness, δ , is small relative to the support particle diameter;
- 5) the micro kinetics for substrate elimination in the biofilm can be described by the Monod expression.

The model seeks to differentiate between three possible operating situations, i.e., first order kinetics, zero order kinetics with reaction rate limitation and zero order kinetics with diffusion rate limitation. The theoretical dependence of the gas phase pollutant concentration with respect to filter height for each possible situation, for a bottom inlet biofilter in which the microbial biomass remains constant, is given by:

- 1) $C_g/C_{gi} = \exp(-hK_1/m_i U_g)$
- 2) $C_g/C_{gi} = 1 - (K_0 h/U_g C_{gi})$
- 3) $C_g/C_{gi} = [1 - (h/U_g) * \sqrt{\{(K_0 D_e a) / (2m_i C_{gi} \delta)\}}]^2$

For downward flow, the same equations can be used by substituting the depth of sample port measured from the inlet (top) of the column for the height, h .

For each given inlet pollutant concentration and air flow rate, representation of the pollutant concentration profiles in the biofilter in the logarithmic, linear and quadratic manners, respectively, will assume a straight line when elimination kinetics correspond to any of the possible theoretical situations that have been proposed.

Correlation coefficients for linearised profiles based on the three kinetic models proposed for the four experi-

Table 1. Correlation coefficients, r , for linearised profiles according to the biophysical models. Logarithmic, linear and quadratic regressions correspond to: 1) first order kinetic, 2) zero order kinetic: reaction limitation, 3) zero order kinetic: diffusion limitation. The regression range was: a) the entire profile; b) from the top to a relative height of 33%; c) from the top to a relative height of 59%

Gas flow	0.149 m ³ h ⁻¹			0.298 m ³ h ⁻¹			0.342 m ³ h ⁻¹			0.468 m ³ h ⁻¹		
Solvent followed	MEK	MIBK	Total	MEK	MIBK	Total	MEK	MIBK	Total	MEK	MIBK	Total
Regression range	c	b	b	b	a	a	b	b	a	a	a	a
1) Logarithmic	0.999	0.902	0.938	0.991	0.968	0.966	0.989	0.998	0.955	0.956	0.961	0.994
2) Linear	0.835	0.841	0.806	0.889	0.932	0.852	0.945	0.996	0.978	0.945	0.992	0.987
3) Quadratic	0.925	0.928	0.926	0.970	0.959	0.924	0.991	0.997	0.988	0.994	0.980	0.999

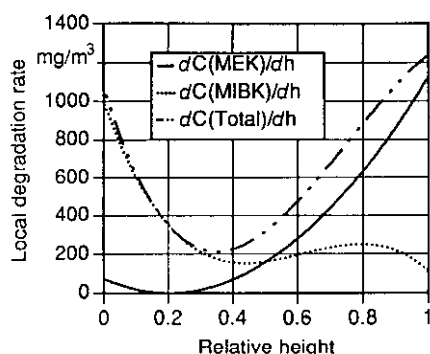


Fig. 8. Local biodegradation activity (expressed in mg m⁻³) in the column with respect to the relative sampling height. The activities are obtained by differentiating the fitted profiles. MEK (—), MIBK (· · · ·), and total activity (· · · · ·). Polluted air flow: 0.342 m³ h⁻¹

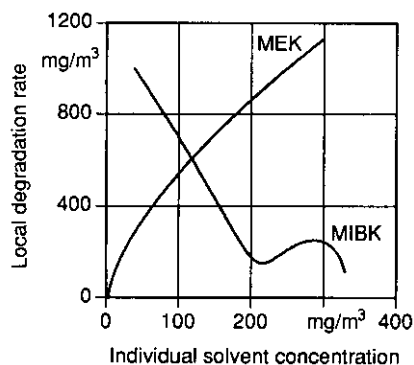


Fig. 9. Local biodegradation activity into the column (expressed in mg m⁻³) with respect to the corresponding gas concentration. Polluted air flow: 0.342 m³ h⁻¹

an air flow rate of 0.468 m³ h⁻¹, each kinetic relationship offers a relatively good correlation for the entire biofilter height, indicating that it is impossible to differentiate between kinetic models on the basis of concentration profiles alone. In order to elucidate the overall kinetics that apply to the operation of the biofilter under investigation, it will be necessary to either determine solvent vapour elimination as a function of the inlet solvent vapour concentration [10] or to recirculate a fraction of the biofilter outflow [11].

In addition to modelling, the evaluation of local activities in biofilters can also provide valuable kinetic data. Such activity evaluations can be achieved by differentiating polynomial profile fits. Using this approach, local degradation rates are plotted against relative height in the biofilter for MEK, MIBK and total solvent, respectively, in Fig. 8 and against individual solvent concentration for MEK and MIBK, respectively, in Fig. 9. Figure 9 clearly indicates that the rate of MEK elimination increases with increasing MEK concentration, whilst the rate of MIBK elimination decreases to low level even at moderate concentrations. However, such results must be interpreted with caution because of both uneven distribution of the active biofilm throughout the biofilter and possible effects on elimination that emanate from the mixture of solvent vapours that was subject to treatment.

5 Conclusions

Biofilters of the type employed in the present investigation are extremely complex systems. Their optimisation for the treatment of either single or multiple carbonaceous pollutants in the vapour state in air streams requires markedly improved system descriptions and much more detailed knowledge concerning elimination kinetics for both single and multiple pollutants. As far as biofilter performance is concerned, it is of particular importance to ascertain the rôle of pollutant solubility in water when pollutant vapours are biodegraded by biofilms contacted with humid air streams.

mental air flow rates used are given in Table 1. At the lowest air flow rate, 0.149 m³ h⁻¹, none of the proposed kinetic relationships satisfy the experimentally generated profiles. At air flow rates of 0.298 and 0.342 m³ h⁻¹, it is impossible to differentiate between the goodness of fit between the three proposed kinetic relationships, whilst at

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