The removal of methyl ethyl ketone in an essentially gaseous-phase biofilm bioreactor: aspects of dynamic behavior and the influence of operating characteristics

Hocine Ali-Khodja

Département de Chimie, Faculté des Sciences, Université Mentouri, Constantine 25017, Algeria

ABSTRACT. In the work reported here, the removal of methyl ethyl ketone from waste gases in a novel bioreactor type was studied experimentally within the pollutant loading range of 0.35 to 16.2 kg m_r^{-3} d^{-1}. The solvent eliminating performance of the bioreactor described in this paper is reflected by a maximum methyl ethyl ketone elimination capacity $EC_{max} = 4.2$ kg m_r^{-3} d^{-1}. The effect of the pH was studied. A nutritive medium with pH=7.3 appeared to give better system performances than a solution with pH=6.8. Moreover, the effects of air and liquid flow rates were studied. The reduction of either the gas or liquid flow rates led to a significant improvement of the degradative capacity of the system suggesting mass transfer limitation. Finally, selected aspects of the dynamic behavior of the dry tubular bioreactor have been investigated.

1 INTRODUCTION

Biodegradation of solvent vapors may offer a cost-effective way to comply with increasingly strict air emission standards. Air emissions of solvent vapors are the subject of stringent environmental regulations. Biological systems for elimination of volatile organics have been explored quite extensively by several authors (Ottengraf, 1986; Deshusses and Hamer, 1993).

Previous work dealing with a novel bioreactor type has recently been carried out by Agathos *et al*. (1997). Such a bioreactor has been described elsewhere (Ali-Khodja, 2005). In this study, the elimination performance of the essentially gas-phase reactor is described in relation to the influence of the liquid medium pH within the pollutant loading range of 0.35 to 16.2 kg m_r^{-3} d^{-1} and other process variables of practical interest, namely the influence of the liquid and air flow rates.

The study of both steady-state and transient elimination of the solvent is also carried out and provides data concerning the response of the bioreactor exposed to perturbations in both pollutant loads and air flow rates.

2 MATERIALS AND METHODS

The tubular biofilm bioreactor, its atomizer, the gas feed, the inoculum, the medium, the analysis of MEK in the gas and liquid phases were described elsewhere (Ali-Khodja, 2005).

3 RESULTS AND DISCUSSION

3.1 The influence of the liquid medium pH

The effect of the composition of the liquid medium that is fed to the micro-organisms was therefore investigated through the use of two nutritive media with slightly different pH values and by comparing the elimination capacity for varying MEK loadings ranging from 0.35 to 16.2 kg m_r^{-3} d^{-1}. As the biofilm was subject to sloughing according to a recurrent cycle of about 6 to 9 days, the two sets of experiments were carried out at two consecutive cycles so that the biofilm could grow subject to a given liquid medium pH while all other conditions were kept constant. Table 1 lists the compositions of the liquid media used in our experiments. Four different solvent loadings were applied each day allowing the bioreactor to stabilize during two hours between two consecutive mass balances; a quite stable bioreactor performance was observed once the inner surface of the tubular reactor was evenly colonized so that the spreading of all experiments for a given liquid medium over four to five days did not affect significantly the results. In Figure 2, the steady-state elimination capacity is plotted versus the pollutant loads for liquid media pH of 7.3 and 6.8. The experimental data in this figure show a slightly better performance of the bioreactor with medium A up to an organic loading of 8 kg m_r^{-3} d^{-1}. This tendency is reversed in favor of medium B between 8 and 14 kg m_r^{-3} d^{-1}. It is possible that as the biofilm grew, it was stressed in the lower layers by oxygen deficiency and went through a state of adjustment from a strictly aerobic mode to one that was both aerobic and anaerobic (Hoen and Ray, 1973). As the adjustments were occurring, the MEK utilization could have been impaired for a time until the communities adjusted for the new regime of interactions between aerobes and anaerobes. The same trend in substrate removal rates occurred with medium B at MEK loads ranging between 10 and 14 kg m_r^{-3} d^{-1} but with a lesser magnitude. A critical solvent loading of 12.8 kg m_r^{-3} d^{-1} was observed for medium B whereas with medium A, the biofilm stayed uninhibited at 16 kg m_r^{-3} d^{-1} and degraded 3.4 kg m_r^{-3} d^{-1}. We clearly see that the curves follow two opposite patterns of variation at MEK loads higher than 14 kg m_r^{-3} d^{-1}. This suggests the existence of acidic conditions in the biofilm grown under medium B while the biofilm grown under medium A was capable of withstanding MEK loads of at least 16.2 kg m_r^{-3} d^{-1}. This could be attributed in part to the better biofilm growth observed with medium A and the stronger pH of the latter.

Table 1. Composition of the two media fed to the bioreactor at the beginning of two consecutive cycles.

Essential nutrients	Concentrations	
	Medium A (mM) pH = 7.3	Medium B (mM) pH = 6.8
$(NH_4)_2SO_4$	27.5	27.5
$Na_2HPO_4.2H_2O$	50	50
KH_2PO_4	25	25
NH_4NO_3	27.5	-

3.2 The influence of the air flow rate on the removal characteristics

In Figure 3 the measured volumetric elimination capacity is plotted in relation to the inlet volumetric load for the two air flow rates studied. From this figure, the bioreactor seems to be more effective at lower flow rates than at higher flow rates. Ottengraf *et al.* (3) and Ottengraf and Van der Over (4) had previously proved that such differences were the result of diffusion limitation in the biolayer. The figure also shows that the critical volumetric load, indicating the transition from the diffusion to the reaction limited regime in the bioreactor concerned, is of the order of 9.5 kg m_r^{-3} d^{-1} at 1000 l h^{-1}, whereas at 500 l h^{-1} the transition is not yet reached at a load of 12.5 kg m_r^{-3} d^{-1}.

In terms of conversion of MEK, Figure 4 demonstrates that the pollutant removals are higher at the lower air flow rate particularly at low pollutant loads. The elimination efficiencies get close at 10.0 kg m_r^{-3} d^{-1}. One clearly sees an increase in elimination capacity parallel to the increase in inlet pollutant load and a corresponding decrease in percentage removal for both air flow rates. At 500 l h^{-1}, 93 % and 86 % removals are observed for inlet concentrations of 1.7 and 3 g/m^3 corresponding to pollutant loadings of 1.1 and 2.2 kg m_r^{-3} d^{-1} respectively, whereas, at 1000 l h^{-1}, removal rates of 70 % and 63 % were noted for inlet MEK concentrations of 0.83 and 1.54 g m^{-3} corresponding to 1.1 and 2.0 kg m_r^{-3} d^{-1} respectively. This highlights the favorable effect of increasing the gas residence time in the reactor. Indeed, doubling the latter from 68 seconds to 136 seconds while doubling at the same time the pollutant inlet concentrations resulted in increasing the volumetric degradation capacity by at least 20 %.

A significant reduction in the outlet MEK gaseous concentration is clearly evident in Figure 5 at the lower air flow rate. For the latter, breakthrough of solvent vapor occurred at an inlet concentration of 3 g m^{-3}, whereas in the case of the higher air flow rate, incomplete conversion is observed for all inlet concentrations tested. For comparative purposes, it is worthwhile to note that Deshusses (1994) observed MEK breakthrough values of 0.65 and 2.00 g m^{-3} for air flow rates of 400 and 200 l h^{-1} respectively during the solvent passage through a compost-based biofilter.

3.3 The influence of the liquid flow rate

Apart from the optimal conditions for the biological reaction and the mass transfer of gaseous pollutant from the gas phase to the biofilm, the liquid flow may also influence the formation and the thickness of the biofilm (Diks and Ottengraf, 1991) and thus the system performance.

The influence of the liquid flow rate on the elimination capacity was therefore investigated for pollutant loads ranging from 2.2 to 15.4 kg m_r^{-3} d^{-1} at 0.15 and 0.9 l h^{-1}. The gas flow rate was equal to 1000 l h^{-1} as it corresponded to the standard conditions. It can be observed from Figure 6 that the elimination capacity increases at a lower liquid flow rate for pollutant loads higher than 4.0 kg m_r^{-3} d^{-1}; the average increase is of the order of 0.8 kg m_r^{-3} d^{-1}, corresponding to an average enhancement of the removal rate equal to 33 %. The observed increase of the elimination capacity at the lower liquid flow rate could be explained by the better mass transfer of the solvent through the liquid phase due to the existence of a thinner liquid film covering the surface of the biofilm. In Figure 7 and 8, the MEK outlet concentrations in the gas and the liquid phases are plotted versus the inlet concentrations. It is shown that the pattern of variation of the outlet concentrations is the same for both liquid flow rates in both phases. While the solvent concentrations do not differ much in the gas phase, they differ quite significantly in the liquid phase for the two liquid flow rates. The reaction rate is lowered because of an increased resistance to mass transfer at the higher liquid flow rate.

The critical pollutant load does not seem to vary at the two liquid flow rates although a decrease of the biofilm thickness due to sloughing has been observed as a result of an increased shear stress by the liquid film.

3.4 Dynamic behavior

This section deals with some typical responses that may occur in real systems, particularly step changes in solvent loadings and in air flow rates. Experiments were carried out for a period of 25 hours in which the air flow rate and/or the applied solvent loading were varied stepwise in order to examine the transient response of the tubular bioreactor. Usually, about 2 to 3 hours were needed in order to reach a new steady state. The experiment reported in Figure 9 combines both airflow rate and pollutant loading step changes according to the scheme shown in Table 2.

After the second step change at 5.3 hours, corresponding to an increase of the MEK loading from 2.2 to 4.0 kg m_r^{-3} d^{-1} at an air flow rate of 500 l h^{-1}, a three-hour long period was observed before equilibrium of the system was recovered. This phenomenon can be explained on the basis that with an increase in pollutant loading, absorption occurs because the biofilm concentration becomes temporarily lower than the equilibrium value (Deshusses *et al.*, 1996) and leads to a temporary apparent elimination capacity of 3.0 kg m_r^{-3} d^{-1} which drops to 2.7 kg m_r^{-3} d^{-1} at steady state. However, the lowest intermediate elimination capacity reached was 2.5 kg m^{-3} d^{-1}. An increasing biodegradative activity of the biofilm required a period for adaptation for the biomass reactivation.

Table 2. Scheme representing MEK step changes.

Time of change (hours)	MEK loading (kg m_r^{-3} d^{-1})	Air flow rate (l h^{-1})
0	1.11	500
2.3	2.15	500
5.3	4.00	500
9	3.55	1000
10	1.05	1000
14.9	1.95	1000
17.4	6.53	500
18.7	8.20	500
21.4	10.06	500
23.4	12.56	500

At 9 hours, the organic load was decreased from 4.0 to 3.5 kg m_r^{-3} d^{-1} while the airflow rate was doubled to 1000 l h^{-1}. A temporary decrease of the elimination capacity is predicted because of the combined flow rate increase and inlet concentration decrease. In this case, the direction of the diffusion flux in the biofilm is reversed. Desorption occurs because the biofilm concentration becomes temporarily greater than the equilibrium value.

It is interesting to note that at the lower air flow rate, the unsteady-state performances were significantly better than at 1000 l h^{-1}. The removal rates varied between 32 % and 70 % for a solvent load of 1.0 kg m^{-3} d^{-1} at 1000 l h^{-1}, whereas at 500 l h^{-1}, they ranged from 82 % to 93 %.

At 17.4 hours, the air flow rate was maintained constant at 500 l h^{-1}, *i.e.*, a volumetric air flow rate of 26.3 m^3 m^{-3} h^{-1} while MEK was varied stepwise in the inlet stream. Increasing MEK loadings of 6.5, 8.2, 10.0 and 12.5 kg m^{-3} d^{-1} were applied at 17.4, 18.7, 21.4 and 23.4 hours respectively. In all cases, a volumetric degradation capacity lower

than the corresponding value for stationary operation was observed some time before steady state was reached. This indicates that the biomass was probably temporarily inhibited as a result of pollutant shock and required the usual period for reactivation. However, the decline in degree of conversion was not proportional to the load applied. The corresponding degrees of conversion measured were equal to 43 %, 38 %, 31 % and 33 % respectively. The maximum volumetric degradation capacity corresponded to an applied load of 12.5 kg m^{-3} d^{-1}, and was equal to 4.2 kg m^{-3} d^{-1}.

4 CONCLUSIONS

Experimental behavior of a novel bioreactor type was described and discussed. The effect of medium pH was examined. A nutritive solution with pH = 7.3 produced a better pollutant degrading biomass than a solution with pH = 6.8. In fact, it produced a thicker biofilm and led to an increase of both the removal capacity and the critical MEK load. Step changes in pollutant loads and/or air flow rates provided interesting information and the particularly important phenomena of absorption and desorption. A period of 2-3 hours was necessary to reach steady-state after perturbation. The reduction of the air flow rate from 1000 l h^{-1} to 500 l h^{-1} led to better removal rates both in the steady-state and the dynamic situations. This was an expected result since reducing the air flow rate by half led to doubling both the inlet MEK concentration for a given pollutant load and the gas residence time. Moreover, the critical pollutant load increases markedly with a 50 % reduction in the air flow rate. Finally, the increase in the elimination capacity of the bioreactor following a decrease of the liquid flow rate emphasizes the role of the liquid phase and suggests its involvement for mass transfer limitation. New data concerning the non steady-state response of the biofilm bioreactor reflecting real situations was also presented and indicated the relatively rapid bioreactor response to changing solvent loads and air flow rate.
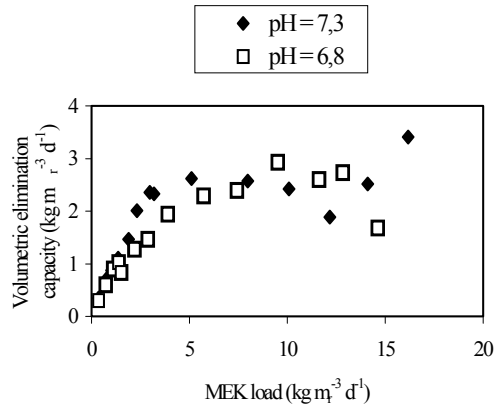
Figure 2. The effect of the pH on the elimination capacity
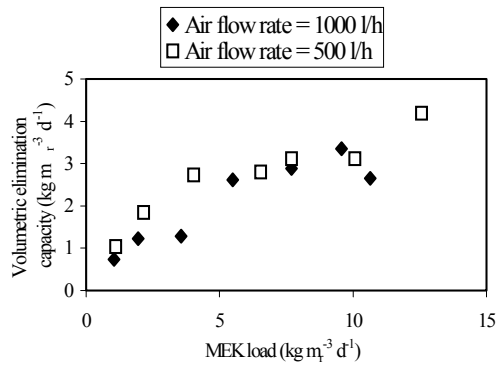

Figure 3. The elimination capacity curves versus the MEK load determined at 500 l/h
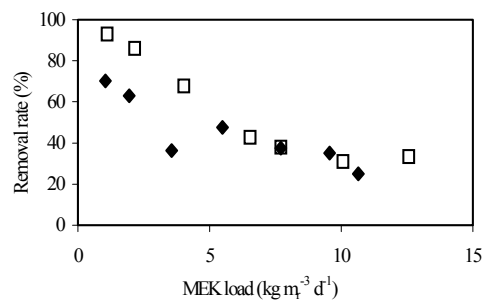and 1000 l/h (liquid flow rate = 0,5 l/h)

Figure 4. The effect of the air flow rate on the MEK removal rate
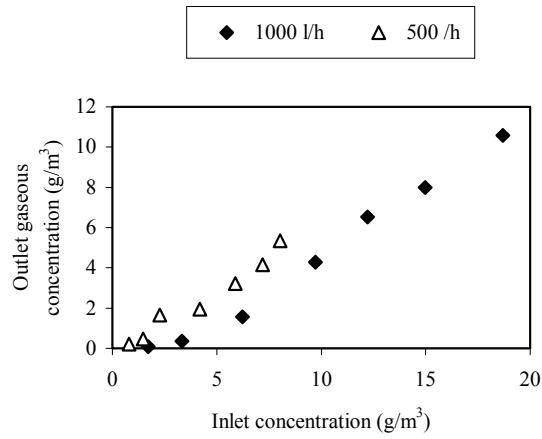at 500 l/h and 1000 l/h
(liquid flow rate = 0,5 l/h)

Figure 5. Outlet gaseous concentrations versus inlet gaseous concentrations
for the elimination of MEK at two different air flow rates, 500 l/h and
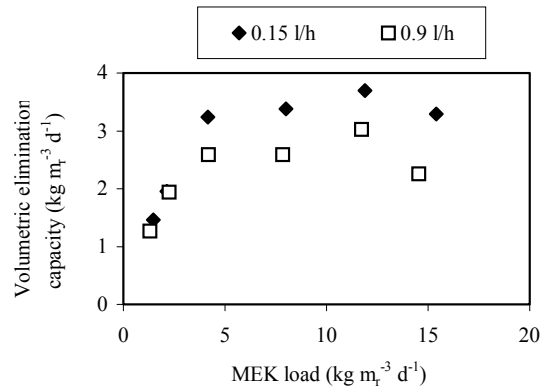1000 l/h (liquid flow rate = 0,5 l/h)

Figure 6. The elimination capacity curves at liquid flow rates of 0,15 l/h and
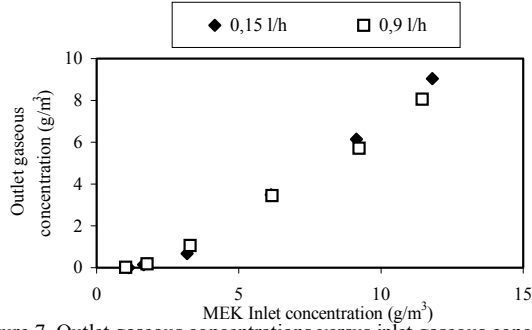0,9 l (air flow rate = 1000 l/h)

H. ALI-KHODJA

Figure 7. Outlet gaseous concentrations versus inlet gaseous concentrations for the elimination of MEK at two different
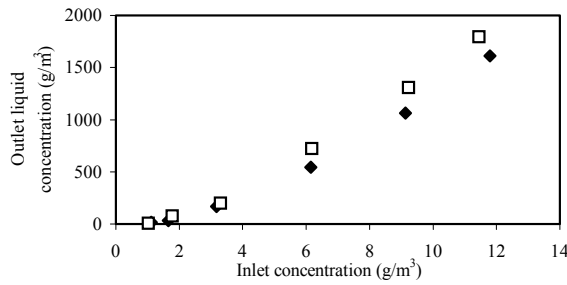liquid flow rates, 0,15 l/h and 0,9 l/h (air flow rate = 1000 l/h)

Figure 8. Outlet liquid concentrations versus inlet gaseous concentrations for the elimination of MEK at two different liquid flow rates, 0,15 l/h and 0,9 l/h (air flow rate = 1000 l/h)
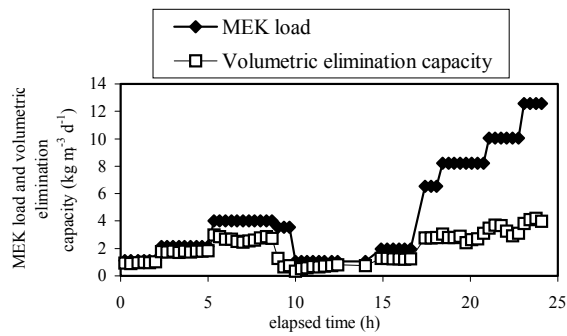

Figure 9. Dynamic behavior of the biofilm bioreactor to step changes
in MEK load and air flow rate

6 REFERENCES
Ottengraf, S.P.P. (1986) Exhaust gas purification. In: Biotechnology. Volume 8 (Rehm, H.J. and Reed, G., Eds) VCH Weinheim, Germany, pp. 426-452.

Deshusses, M.A. and Hamer, G. (1993) The removal of volatile ketone mixtures from air in biofilters. *Bioproc. Eng.* 9: 141-146.

Agathos, S.N., Hellin, E., Ali-Khodja, H., Deseveaux, S., Vandermesse, F. and Naveau, H. (1997) Gas-phase methyl-ethyl-ketone biodegradation in a tubular biofilm bioreactor: microbiological and bioprocess aspects. *Biodegradation.* 8: 251-264.

Thalasso, F., L'Hermite P., Hammami, R., Naveau H.P. and Nyns E-J. (1993) Reactor design for biological gas treatment using the mist foam concept. In: Proc. of the second international symposium on characterization and control of odors and VOC in the process industry. (Verachtert, I.H. and Verstraete, W., Eds), Royal Flemish Society of Engineers, Ostende, Belgium, pp. 419-429.

Ali-Khodja, H. (2005). Comparison of MEK utilization and growth kinetics between batch and fixed-film processes. In: Biotechniques for Air Pollution Control, University of La Coruña Publisher, La Coruña, Spain.

Hoen, R.C and Ray, A.D. (1973). Effects of thickness on bacterial film. *J. Wat. Pollut. Contr. Fed.* 45: 2302-2320.

Deshusses, M.A. (1994) Ph.D. Dissertation, Swiss Federal Institute of Technology, Zurich, Switzerland.

Diks, R.M.M, Ottengraf, S.P.P. (1991) Verification studies of a simplified model for the removal of dichloromethane from waste gases using a biological trickling filter (Part II). *Bioprocess Eng.* 6: 131-140.

Deshusses, M.A., Hamer, G. and Dunn, I.J. (1996) Transient-state behavior of a biofilter removing mixtures of vapors of MEK and MIBK from air. *Biotechnol. Bioeng.* 49: 586-598.