DEGRADATION OF METHYL TER BUTYL ETHER (MTBE) VAPORS BY COMETABOLISM WITH PENTANE IN A BIOFILTER

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ABSTRACT

Degradation of MTBE vapors by cometabolism with pentane using a culture of pentane-oxidizing bacteria (*Pseudomonas aeruginosa*) was studied in a 2.4 liters biofilter. Experimental Elimination Capacity (EC) of pentane of 7 $g.m^{-3}.h^{-1}$ was obtained for an Empty Bed Residence Time (EBRT) of 1.1 hour and inlet concentration of 18 $g.m^{-3}$. For these experimental conditions, EC of MTBE between 0.3 and 0.7 $g.m^{-3}.h^{-1}$ were measured for an inlet MTBE concentration ranged from 1 to 11 $g.m^{-3}$. A kinetic model describing cross-competitive inhibition between MTBE (cosubstrate) and pentane (substrate) was used. Experimental data of removal efficiencies of pentane and MTBE were compared to the theoretical predictions of the model. Despite the fact that the cometabolism is a very complex phenomena, the agreement between theory and experiments was good.

KEYWORDS

Biofilter, vapors, methyl ter-butyl ether, pentane, cometabolism, degradation, modeling.

INTRODUCTION

Biofiltration is a biotechnological method for removal of undesired off-gas components. Up to 1980, biofiltration was mainly used to reduce odor in off-gases. In the early 1980s, the field of application was extended to the removal of many other volatile organic compounds. Biofiltration is a cost-effective method for the removal of a large volume of contaminated air (Devinny *et al.*, 1998). This technology demands low power requirements and the process equipment is simple and generally easy

to operate. In biofiltration, the gas to be treated is forced through a bed packed with material on which microorganisms are attached as a biofilm. Biodegradable volatile compounds diffuse into the biofilm where are subsequently biologically oxidized into less harmful substances like CO_2 and H_2O.

Methyl tertiary butyl ether (MTBE) is one of several fuel oxygenates added to gasoline to improve fuel combustion and reduce the resulting concentrations of carbon monoxide and unburned hydrocarbon. The massive production of MTBE, combined with its mobility, persistence and toxicity, make it an important pollutant. Due to the presence in the aquifer, it has been recently proposed that MTBE be removed from gasoline in California no later than the year 2002.

To this date, very few studies have been conducted in order to find microorganisms able to degrade MTBE and utilize them in biological treatment. Consortia and pure microorganisms have been studied for their ability to degrade MTBE as sole source of carbon and energy in aerobic (Salanitro *et al.*, 1994; Mo *et al.*, 1997) and anaerobic conditions (Mormile *et al.*, 1994). Few studies have addressed the cometabolic degradation of MTBE by pure cultures. In one recent study, Hardison *et al.* (1997) reported degradation of MTBE by filamentous fungus in presence of DEE (diethylether). Steffan *et al.* (1997) studied the biodegradation of MTBE mainly by three propane oxidizing strains (ENV421, ENV425 and *Pseudominas putida*). Garnier *et al.* (1999) measured various parameters of the kinetic degradation of MTBE in presence of pentane by *P. aeruginosa* in batch system. In a pilot scale biofilter, biodegradation of MTBE vapors were reported (Eweis *et al*, 1998; Fortin and Deshusses, 1999).

The aim of this study is to investigate the degradation of MTBE vapors by cometabolism with pentane using a culture of pentane-oxidizing bacteria. The study was carried out with a 2.4 l biofilter packed with a mineral support (vermiculite). A model study was conducted to understand and predict cometabolic degradation in presence of pentane. Its predictions were compared with experimental results obtained from the biofilter.

THEORY

The theoretical model presented in this section was based on that proposed by Ottengraf and van der Oever (1983). To describe cross-competitive inhibition between MTBE (cosubstrate) and pentane (substrate) a kinetic model was used (Arcangeli *et al.*, 1997).
The differential equation describing the concentration of the compound i (Si) inside the biolayer at steady-state conditions is :

$$Dei\frac{d^2Si}{dx^2} = ri \qquad (1)$$

Dei: coefficient of effective diffusion of the product i (m^2/s)
ri: reaction rate of the product i ($g.m^{-3}.s^{-1}$)
i : pentane (p) or MTBE (m)

Boundary conditions will be:

x=0	$Si = C_{gi}/m_i$
x=δ	$d\,Si/dx = 0$

with: Cgi: gas concentration ($g.m^{-3}$), δ biofilm thickness (m) and m_i: distribution coefficient

The reaction rate of pentane, which supports the biomass growth, can be described by eq. 2 assuming a competitive inhibitory effect of the cosubstrate. The inhibition coefficient of the competitive inhibitor is approximated by its single-substrate half-saturation coefficient.

$$r_p = k_s(pent).X_{fa}.\frac{S_p}{S_p + K_s(pent).\left(1+\frac{S_m}{K_s(MTBE)}\right)} \qquad (2)$$

MTBE cannot serve as a source of carbon for cell synthesis (Garnier *et al.*, 1999) but its transformation is possible when pentane is supplied in the reactor. Then, the biodegradation of MTBE occurs only in the presence of pentane. MTBE degradation is described by eq. 3, considering the competitive inhibition and the stimulating effect of pentane.

$$r_m = k_s(MTBE).X_{fa}.\frac{S_m}{S_m + K_s(MTBE).\left(1+\frac{S_p}{K_s(pent)}\right)}.\left(\frac{S_p}{S_p + K_s(pent)}\right) \qquad (3)$$

where

kx (i) is the maximum substrate utilization rate in g of i .g(biomass)$^{-1}$.s^{-1},
Xfa is the active biomass concentration in $g.m^{-3}$ of biolayer,
Ks(i) is the half-saturation constant of i in $g.m^{-3}$.

The kinetic model considers two biomass: an active biomass, X_{fa}, capable of degrading pentane and MTBE, and an inactive biomass, which includes dead cells and exopolymers (EPS) unable to degrade these compounds (Pineda *et al.*, 1996). These two biomass form the total biomass (Xf).

From a differential mass balance in the gas phase, Cgi can be calculated as a function of the height h in the filter bed, according to (Ottengraf and van der Oever, 1983):

$$-Ug\frac{dCgi}{dh} = Ni.As \qquad (4)$$

where Ni (in $g/m^2/s$) is the substrate flux into the biolayer, As the interfacial area per unit of reactor volume (in m^2/m^3), h the distance from the biofilter entrance (in m) and Ug the superficial gas flow rate (in m/s).

Expression of Ni is given by the Fick law:

$$Ni = -Dei\left(\frac{dSi}{dx}\right)_{x=0} \qquad (5)$$

MATERIALS AND METHODS

Inoculum and mineral medium

A bacteria identified as *Pseudomonas aeruginosa* and able to degrade MTBE when cometabolized in presence of pentane was isolated from soil samples contaminated from gasoline (Garnier *et al.*, 1999). The isolated strain was enriched and two liters of medium were prepared for the inoculation.

Biofilter and packing material

A three-stage biofilter consisted on a cylindrical glass column with an inner diameter of 7.8 cm, having a height of 1 meter (Dupasquier, 1998). Each filter stage was packed with a mineral support (vermiculite) and supported by a plate to ensure a homogeneous of bed volume. The active filter bed height was 0.5 m and packing density was 110 g of dry vermiculite per liter. Medium size of vermiculite particles was around 4.11 mm. Biofilter temperature was maintained between 29°C and 31°C. Operating conditions of the biofilter are presented in the table 1.

Inlet MTBE concentration in $g.m^{-3}$	0.5 to 13	Reactor volume in L	2.36
Inlet pentane concentration in $g.m^{-3}$	18	Temperature in °C	30
Air flow in $L.h^{-1}$	2.1	EBRT in h	1.1

Table 1: Operating conditions of the biofilter

Pollutants introduction

Pentane from a 1 % concentration pressured tank was introduced directly to the reactor (lower pentane concentrations than 1 % were obtained by mixing pentane with compressed air) after being saturated with water vapor by sparging through a column containing water. The main air stream was controlled by a mass flow meter. A small air flow was sparged into 0.5L bottle containing MTBE and mixed with the air contaminated by pentane before entering to the top of the reactor. The MTBE bottle was put into a refrigerator system to control temperature variations.

Analysis

Pentane and MTBE concentrations in the gas phase were determined by gas chromatography. A 250 ml-air-tight syringe was used for taking air samples at the inlet, outlet, and two other levels along the biofilter bed. These samples were injected into a Hewlett-Packard 5890 chromatograph fitted with a 30 m CP WAX 52 CB column and operated isothermally at 40°C. The detection limit was about 5 mg of pollutant per cubic meter of air.
Total biomass was determined by Lowry method.

Definitions

Elimination capacity (EC) of the biofilter was determined as the concentration difference between inlet (Cgin) and (Cgout) divided by the empty bed residence time. EC is expressed as $g_{\text{of pollutant}}\ m^{-3}_{\text{of biofilter}}\ h^{-1}$. Removal efficiency (Ef) is defined as the ratio between the concentration difference and the inlet concentration (Cgin).

Determination of the model parameters

The determination of different parameters was required to solve the model. Kinetic parameters, Ks (pent), Ks (MTBE), kx (pent) and kx (MTBE) were previously determined by Garnier *et al.* (1999) from batch experiments. To measure As, δ, Xf and Xfa a model of biolayer presented by Pineda *et al.* (1996) were used.
The coefficient of effective diffusion (Dei) of the products (Pentane and MTBE) in the biolayer was calculated by Fan correlation (Fan *et al.*, 1990).
Table 2 presents the parameter values used for solving the model equations.

De, pent (m^2/s)	$1*10^{-9}$	h (m)	0.495
De, MTBE (m^2/s)	$0.9*10^{-9}$	δ (m)	0.000387
kx (pent) (g/g db/s)	$58.4*10^{-9}$	As (m^2/m^3)	284
kx (MTBE) (g/g db/s)	$5.53*10^{-9}$	Xf (g db/m^3 biofilm)	28300
Ks (pent) (g/m^3)	0.8517	Xfa (g db/m^3 biofilm)	2264
Ks (MTBE) (g/m^3)	185	T (°C)	30

*db: dry biomass

Table 2 : Parameter values of the model

RESULTS AND DISCUSSION

A series of experiments were conducted by conserving the inlet pentane concentration (around 18 $g.m^{-3}$) and the EBRT (1.1 h) constant. Only the inlet MTBE concentration was varied.
Figures 1 and 2 represent pentane and MTBE concentration profiles along the biofilter for inlet MTBE concentrations of 4.8 and 11 g. m^{-3}, respectively. At the steady state condition, the slope of MTBE concentration profile was low and consequently its EC (around 0.6 $g.m^{-3}.h^{-1}$). However, it was clear that MTBE was degraded by cometabolism with pentane. The EC of MTBE was much lower than the ECs reported by Eweis *et al.* (1998) (EC max = 15 $g.m^{-3}.h^{-1}$) and from Fortin and Deshusses (1999) (EC max = 50 $g.m^{-3}.h^{-1}$) in biofilters. Both works have reported that MTBE is completely mineralized by their consortia. For the pentane, the degradation kept on being high and its EC was around 7 $g.m^{-3}.h^{-1}$. For the two products, the relation between the concentration and the biofilter height was linear. This behavior indicates that rates of degradation of MTBE and pentane were limited by the biological reaction. The mathematical model predicts well the experimental profiles of pentane and MTBE concentration with the height of biofilter. Errors of EC pentane and MTBE prediction were 3.7% and –13.2 % (Fig. 1) and –8.5 % and 23.7 % (Fig.2).

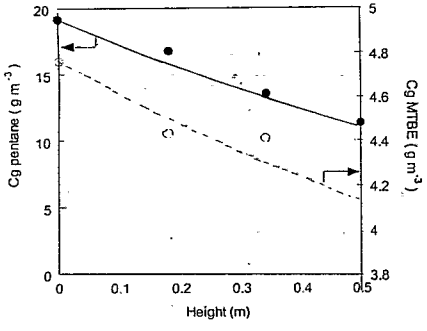

Figure 1: Predicted and experimental profiles of the pentane and MTBE concentrations in the biofilter for pentane inlet concentration of 19 $g.m^{-3}$ and MTBE inlet concentration of 4.8 $g.m^{-3}$. Experimental values (•, pentane) (o, MTBE). Model predictions (—, pentane) (-----, MTBE).

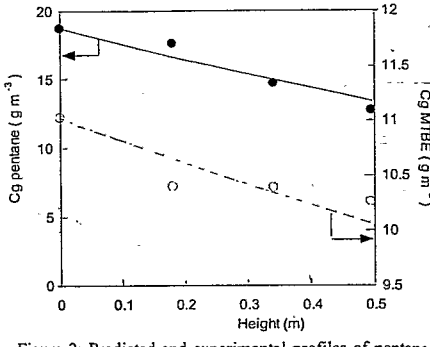

Figure 2: Predicted and experimental profiles of pentane and MTBE concentrations for pentane inlet concentration of 18 $g.m^{-3}$ and MTBE inlet concentration of 11 $g.m^{-3}$. Experimental values (•, pentane) (o, MTBE). Model predictions (—, pentane) (-----, MTBE).

To further understand it, influence of the inlet MTBE concentration on the Ef of pentane and MTBE was studied from model predictions. The results presented in the figure 4 show that the Ef of pentane varies little with the inlet pentane concentration. It decreases slowly when its concentration increases. The most interesting is the fact that the obtained curve is linear. As the removal efficiency (Cgin-Cgout) / Cgin varies along a law in 1 / Cgin,pent, it proves that the outlet concentration Cgout is proportional to Cgin. Moreover, the Ef of MTBE increases linearly with the inlet pentane concentration. Then, Ef of MTBE is proportional to this concentration and so it is an evident proof of the degradation of MTBE cometabolized by pentane.

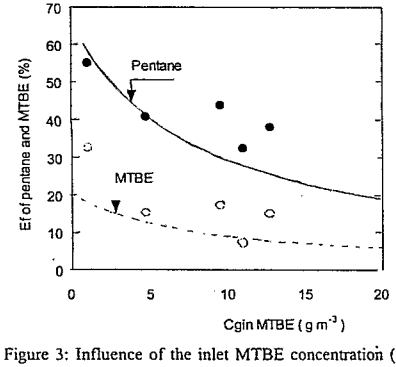

Figure 3: Influence of the inlet MTBE concentration (Cgin) on the removal efficiencies (Ef) of pentane and MTBE. Model predictions (—, pentane) (-----, MTBE). Experimental values (•, pentane) (o, MTBE).

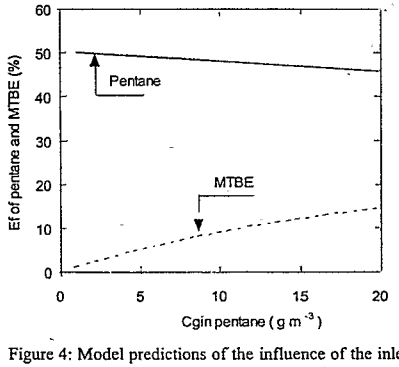

Figure 4: Model predictions of the influence of the inlet pentane concentration (Cgin, pent) on the removal efficiencies (Ef) of pentane (—) and MTBE (----).

The cometabolism of MTBE by *P. Aeruginosa* was shown to be slow process as compared to systems where mineralization occurs. Nevertheless, the system can be optimized by increasing the biomass and operating conditions.

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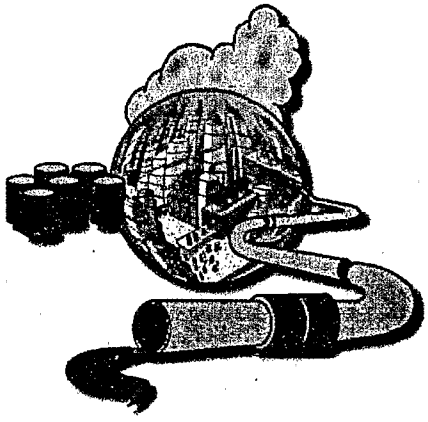
PROCEEDINGS



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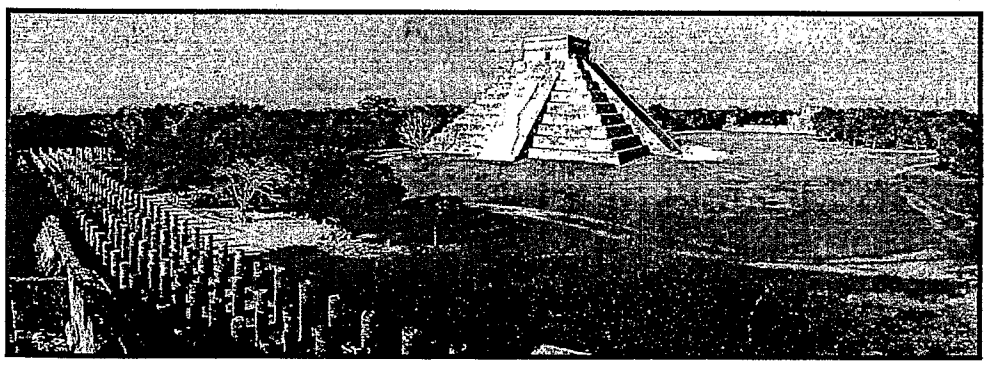

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