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 CO₂ and H₂O.

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 hydrocarbons. 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 by pure cultures. In one recent study, Hardison et al. (1997) reported degradation of MTBE by filamentous fungus in presence of DEE (diethyl ether). Steffan et al. (1997) studied the biodegradation of MTBE mainly by three propane oxidizing strains (ENV421, ENV425 and Pseudomonas putida). Gamier 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 conducted with a 2.4 I 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:

\[ \text{Dei} \frac{d^2S_i}{dx^2} = ri \]  

(1)

Dei: coefficient of effective diffusion of the product i (m²/s) 
ri: reaction rate of the product i (g.m⁻¹.s⁻¹) 
i : pentane (p) or MTBE (m)

Boundary conditions will be:

\[ x=0 \quad S_i = C_{0,i}/m_i \]
\[ x=\delta \quad dS_i/dx = 0 \]

with: C₀i: gas concentration (g.m⁻³), δ biofilm thickness (m) and mᵢ: 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.

\[ r_p = \frac{k(p)X_o}{S_p + K_i(p)\left(1 + \frac{S_p}{K_{MTBE}}\right)} \]  

(2)

MTBE cannot serve as a source of carbon for cell synthesis (Gamier 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.

\[ r_m = \frac{k(MTBE)X_o}{S_m + K_i(MTBE)\left(1 + \frac{S_m}{K_{MTBE}}\right)} \left(1 + \frac{S_p}{K_{MTBE}}\right) \]  

(3)

where

\[ k_i (i) \text{ is the maximum substrate utilization rate in g of } i \text{ g (biomass)}^{-1} \text{ s}^{-1}, \]
\[ X_o \text{ is the active biomass concentration in g.m}^{-²} \text{ of biolayer}, \]
\[ K_S (i) \text{ is the half-saturation constant of } i \text{ in g.m}^{-²}. \]

The kinetic model considers two biomass: an active biomass, Xₐ, 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 (Xₐ).

From a differential mass balance in the gas phase, C₀i can be calculated as a function of the height h in the filter bed, according to (Ottengraf and van der Oever, 1983):

\[-U_g \frac{dC_{0,i}}{dh} = N_i.A_{s} \]  

(4)

where Ni (in g/m²/s) is the substrate flux into the biolayer, A_s the interfacial area per unit of reactor volume (in m²/m³), h the distance from the biofilter entrance (in m) and U_g the superficial gas flow rate (in m/s).

Expression of Ni is given by the Fick law:
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. 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 ratios 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 8.5% (Fig. 1) and 13.2% and 23.7% (Fig.2).

Definitions
Elimination capacity (EC) of the biofilter was determined as the concentration difference between inlet (C_in) and (C_out) divided by the empty bed residence time. EC is expressed as g of pollutant.m⁻³ of biofilter.h⁻¹. Removal efficiency (EF) is defined as the ratio between the concentration difference and the inlet concentration (C_in).
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.

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.

REFERENCES


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WASTE MINIMISATION AND END OF PIPE TREATMENT IN CHEMICAL AND PETROCHEMICAL INDUSTRIES

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