GAS TREATMENT IN TRICKLE-BED BIOFILTERS: A MODELING APPROACH AND EXPERIMENTAL STUDY

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ABSTRACT

The objective of this paper is to define and validate a mathematical model that describes the physical and biological processes occurring in a trickle-bed air biofilter for waste gas treatment. The model assumes a two phase system, quasi-steady state and one limiting substrate. Experimental data from the biodegradation of toluene in a pilot system with four packed bed reactors, are used to test the validity of the model. The unknown biofilter variables are estimated using a non-linear parameter estimation technique. Using these parameter values, simulations were carried out for different operational conditions, and the model predictions were compared to experimental data.

Keywords: trickle-bed biofilter, mathematical model, VOC, waste gas treatment, biofiltration.

INTRODUCTION

Biofiltration as a control technology for VOC laden exhaust gases continues to receive attention in research and development arenas. A biofilter consists of a packed bed of organic or synthetic materials on which microbial films are supported. Degradable pollutant species in a waste gas pass through a biofilter, diffuse through these microbial films and are then consumed. Since pollutant degradation occurs at normal temperatures and pressures, biofiltration represents a potential energy efficient technology in comparison to traditional physical and chemical methods of control (e.g., thermal incineration, carbon adsorption). However, biofilters are essentially living pollution control systems, subject to dynamic changes. This characteristic has hindered the widespread application of biofiltration in the United States, where regulatory requirements typically stipulate *continuous* compliance with an emissions limitation or destruction efficiency. To help develop biofiltration as a viable technology able to meet these regulatory constraints, much research has focused on understanding their fundamental chemical and microbiological processes through the development of theoretical models.

The development of biofilter models has occurred in two distinct stages. In the first stage, following the historical application of biofiltration ideas to wastewater treatment, models of water-phase biofilm reactors were developed. In *Biofilms*, Characklis and Marshall (1990) compiled the extensive body of research that has been published on biofilm models and provided detailed descriptions of the processes involved. The first biofilter model, in which the processes of substrate degradation in a biofilm were coupled with equations describing mass transport of pollutants through a packed bed filter, was developed by Jennings et al. (1976). However, this model was developed for a submerged packed bed reactor. Ottengraf and Van der Oever (1983) were the first to adapt this liquid-phase model by changing the transport phase to a gas, thus beginning the second stage of model development for *gas-phase* biofilters. Since then, biofilter models of increasing sophistication have been derived for various system types and applications (Ottengraf, 1986; Diks and Ottengraf, 1991a and 1991b; Hartmans and Tramper, 1991; Utgikar et al., 1991; Ockeloen et al., 1992; Smith, 1993; Shareefdeen et al., 1993; Deshusses et al., 1995a and 1995b). Ottengraf (1986) analytically calculated the efficiency of the biofilm for the limiting cases of first and zero order kinetics for diffusion and reaction limiting degradation. Diks and Ottengraf (1991a and 1991b) considered a simplified model with a three phase system and zero-order kinetics that was numerically solved. Utgikar et al. (1991) used a similar model with first order kinetics expression. Hartmans and Tramper (1991) modeled a trickle-bed bioreactor using a series of identical, ideally mixed tank reactors. Ockeloen et al. (1992) used the same approach as Diks and Ottengraf, but they numerically solved the general model.

Recently, biofilter models have been introduced that account for detailed representations of biofilm degradation mechanisms. Shareefdeen et al. (1993) proposed a biofilter model for a single component waste stream that accounted for rate limitations of oxygen in the biofilms. Smith et al. (1993) developed a two phase trickle-bed biofilter model that incorporated decay and shearing effects

to determine the distribution of biomass in each section of the biofilter. Deshusses et al. (1995a and 1995b) developed a model that accounted for transient processes during start-up and shut-down. Their dynamic model also handles multiple substrate degradation through the incorporation of both noncompetitive and uncompetitive reaction rate expressions.

In this paper, a new theoretical modeling approach is presented for a synthetic media trickle-bed biofilter. The two-phase model developed by Smith (1993) is used as a basis. His steady state model describes the degradation of one limiting substrate (VOC pollutant) in a homogeneous biomass by one type of microorganism species. This approach is enhanced by the addition of a quasi-steady state term that accounts for dynamics of the system. The model has been developed in conjunction with four pilot-scale trickle bed biofilters that use ceramic pellets as the packing medium (Smith et al., 1994). The model presented is assessed against experimental data collected in four trickle-bed biofilters for a variety of operational scenarios. A first set of experimental data were used to estimate the unknown parameters of the biofilter using a non-linear parameter estimation technique. Using these parameter values, simulations were carried out for different operational conditions, and the model predictions were compared with a second set of experimental data. The intent of the model is to facilitate the study of the effects and interdependence of key system variables, such as initial substrate concentration, residence time, temperature, pollutant properties, and system geometry, on biofilter performance. The model can be used for simulation and analysis of the biodegradation process, prediction of biofilter performance and assistance in biofilter design.

METHODOLOGY

Theoretical Model

The theoretical model is developed for a packed bed trickle biofilter employing uniformly shaped solids. Due to the random packing, the flow path for the waste gas is considerably tortuous, and the gas is assumed to be well mixed radially across the biofilter cross section. Consequently, the concentration of contaminant in the bulk gas is assumed to be uniform at any given axial position. The packing solids are modeled as a bed of equivalent spheres sized to have the same volume. All processes are assumed to be uniform across the biofilter cross section, and reactor wall and end effects are negligible. The model considers two phases, the gas phase and the biofilm. A liquid layer, present due to a small and intermittent nutrient solution feed rate, has minimal mass transfer resistance and is disregarded. The temperature in the biofilter and the physical properties of the gas and VOC are assumed to be constant. The variables of interest are the VOC concentration profiles in the biofilm and gas phase, and the biofilm thickness along the reactor. The model is solved for quasi-steady state conditions. First, the biofilm thickness is considered constant to calculate the concentration profiles, and then the biofilm thickness variation with time is computed for a constant concentration profile.

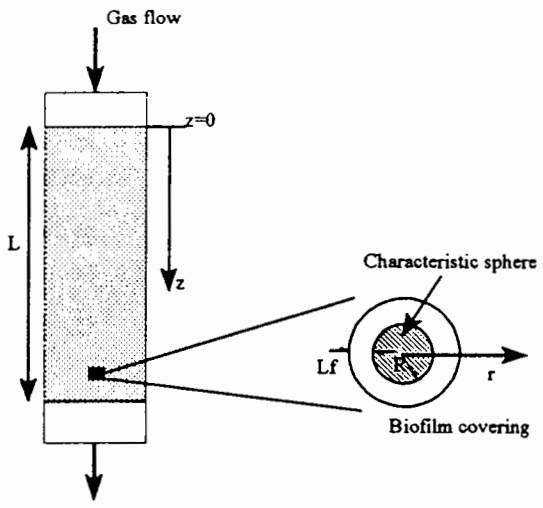

Figure 1. Biofilter system geometry.

In the formulation of the mass balance equations in the biofilter, the following assumptions have been applied: the biofilm is a stagnant liquid; there is no convective transport; axial diffusion is negligible; the microbial growth is described by Monod kinetics; VOC is the only growth limiting substance; and all kinetic parameters and the bacterial density are constant along the biofilter. The biofilter geometry is represented in Figure 1. The mass balance equation for the biofilm phase, expressed in spherical coordinates to account for the curvature of the spheres, is:

$$D_f\left[\frac{d^2C_f}{dr^2}+\frac{2}{r}\frac{dC_f}{dr}\right]=\frac{\mu_m X_f}{Y}\left[\frac{C_f}{K_s+C_f}\right] \qquad (1)$$

where C_f (M/L^3) is the VOC concentration in the biofilm, D_f (L^2/t) is the contaminant diffusivity in the film, assumed to be a fraction, r_d of the contaminant diffusivity in water, D_w, ($D_f = r_d * D_w$), μ_m (t^{-1}) is the maximum bacterial growth rate, Y (M biomass/ M VOC) is the yield coefficient, K_s (M/L^3) is the Monod saturation constant, and X_f (M/L^3) is the film bacterial density.

Radially across the bed, the gas flow and the VOC concentration are uniform, so plug flow can be assumed for the gas phase. As there is no contaminant degradation in the gas phase, the mass balance equation in the biofilm interface can be expressed as:

$$\frac{dC_g}{dz} = \frac{-Ja_f}{u_0} \tag{2}$$

where C_g (ppmv) is the VOC concentration in the gas phase, J (M/L^2 t) is the flux of VOC into the biofilm, a_f (L^{-1}) is the surface area of the bed with biofilm, and u_0 (L/t) is the gas approach velocity, i.e., the gas flow rate divided by the total bed cross sectional area. The surface area per unit volume of the clean packing solids, a_0 (L^{-1}), and with a biofilm growth, a_f (L^{-1}) are given by:

$$a_0 = \frac{3(1-\epsilon_0)}{\phi R}, \qquad a_f = \frac{3(1-\epsilon_f)}{\phi(R+L_f)} \tag{3}$$

where ϕ is the packing solids sphericity, R (L) is the characteristic sphere radius, L_f (L) is the biofilm thickness, and ϵ_f is the actual porosity of the reactor bed with a biofilm. The actual porosity is a function of the clean bed porosity ϵ_0, the clean bed surface area, and the biofilm thickness:

$$\epsilon_f = \epsilon_0 - a_0 L_f \tag{4}$$

The boundary conditions necessary for equation (1) are derived by assuming that there is no flux of contaminant into the surface of the packing solids, and that the concentration of VOC in the biofilm and in the gas phase are in equilibrium defined by Henry's law:

$$@r = R, \quad \frac{dC_f}{dr} = 0 \tag{5}$$

$$@r = R + L_f, \quad C_g = HC_f \tag{6}$$

Assuming a uniform VOC gas concentration at the inlet of the biofilter, the initial condition for equation (2) is:

$$@z = 0, \quad C_g = C_{g0} \tag{7}$$

where C_{g0} is the initial VOC concentration in the gas phase. For equation (2), the flux of VOC in the gas phase in equation (2) is equal to the flux at the biofilm surface:

$$@r = R + L_f, \quad J\left(\frac{PM_v}{R_g T}\right) = J_f = r_d D_w \frac{dC_f}{dr} \tag{8}$$

where P is the system pressure, M_v is the molecular weight of VOC, R_g is the universal gas constant and T is the system temperature.

Since the biofilm thickness is not constant along the biofilter, another equation is needed to characterize its variation. The variation of the biofilm thickness with time is due to the net bacterial growth with steady-state VOC concentration profiles. This assumption of quasi-steady state is valid because the characteristic time of VOC transport and reaction is smaller than the one for bacterial growth. If b (t^{-1}) is the specific combined shear/decay coefficient, this equation is:

$$\frac{dL_f}{dt} X_f = \left(r_d D_w \frac{dC_f}{dr}\bigg|_{r = R + L_f} \right) Y - L_f X_f b$$
$$@\ t = 0 \quad L_f(z,t) = L_{f0} \tag{9}$$

The combined shear/decay coefficient, represents the effects of biomass loss, combining biomass decay and physical shearing, following the formulation of Rittmann (1982). The specific decay coefficient, b_d, is assumed to be constant, and the specific shear rate, b_s, is assumed to be a function of the biofilm thickness.

$$b = b_s + b_d \tag{10}$$

The different existing expressions to define the rate of biofilm detachment, suggest that this process is not very well understood (Peyton and Characklis, 1993). In this case, the shear rate is assumed to be proportional to the shear stress, τ, that is proportional to the interpore gas velocity, $u = u_0/\epsilon_f$.

$$\tau = \beta\left(\frac{u}{\epsilon_f}\right) = \beta\left(\frac{u_0}{\epsilon_f^2}\right) \tag{11}$$

The proportionality constant, β, is chosen to be the default shear rate coefficient, b_s^0, corresponding to the default shear stress, τ^0, when the bed is clean and there is no biofilm, then:

$$\tau^0 = \beta\left(\frac{u_0}{\epsilon_0^2}\right) \quad \rightarrow \quad b_s^0 \propto \beta\left(\frac{u_0}{\epsilon_0^2}\right) \tag{12}$$

Eliminating the constants, the expression for b is:

$$b = b_s^0\left(\frac{\epsilon_0}{\epsilon_f}\right)^2 + b_d \tag{13}$$

The packed bed biofilter model is defined by equations (1)-(9), and (13). These equation can be written in dimensionless form for mathematical simplicity and to reduce the number of model parameters. The new dimensionless variables are:

$$z^* = \frac{z}{L} \quad r^* = \frac{r}{R} \quad t^* = t(b_s^0 + b_d) \quad C_g^* = \frac{C_g}{C_{g0}} \quad C_f^* = \frac{HC_f}{C_{g0}}$$
$$L_f^* = \frac{L_f}{R} \quad L_{f0}^* = \frac{L_{f0}}{R} \quad a_f^* = \frac{a_f}{a_0} \quad b^* = \frac{b}{b_s^0 + b_d} \quad J^* = J\left(\frac{RPM_v H}{r_d D_w R_g T C_{g0}}\right) \tag{14}$$

The governing equations in dimensionless form are:

$$\frac{d^2C_f^*}{dr^{*2}} + \frac{2}{r}\frac{dC_f^*}{dr^*} = A_4\left(\frac{C_f^*}{A_3 + C_f^*}\right) \tag{15}$$

$$\frac{dC_g^*}{dz^*} = -A_1A_2(1-A_6)J^*a_f^* \tag{16}$$

$$@r^* = 1, \quad \frac{dC_f^*}{dr^*} = 0 \tag{17}$$

$$@r^* = 1 + L_f^*, \quad C_g^* = C_f^* \tag{18}$$

$$@z^* = 0, \quad C_g^* = 1 \tag{19}$$

$$@r^* = 1 + L_f^*, \quad J^* = \frac{dC_f^*}{dr^*} \tag{20}$$

$$\frac{dL_f^*}{dt*} = \frac{J^*}{A_5} - L_f^*b^* \tag{21}$$

$$@t^* = 0 \quad L_f^* = L_{f0}^* \tag{22}$$

$$b^* = A_7\left(\frac{A_6}{\epsilon_f}\right)^2 + A_8 \tag{23}$$

$$\epsilon_f = A_6 - A_2(1-A_6)L_f^* \tag{24}$$

$$a_f^* = \frac{(1-\epsilon)}{(1+L_f^*)(1-A_6)} \tag{25}$$

Equations (15) and (16) form a coupled set of non-linear ordinary differential equations, which are solved using the initial and boundary conditions given by equations (17)-(20). Equations (21)-(22) define the variation of the biofilm thickness, and equations (23)-(25) are used to calculate the non-constant biofilter parameters. There are eight dimensionless groups, A_1 to A_8, that are defined in Table 1.

A variable of interest is the concentration of biomass in the reactor, X_r (M/L^3), because it can be measured and it is an indication of the biofilm thickness. X_r is mass of organic matter per volume of reactor, so it varies along the reactor depth, as opposed to biomass density in the biofilm, which is considered constant. The biomass concentration in the reactor can be calculated as:

$$X_r = X_f\, a_f\, L_f = X_f\, R\, a_0\, a_f^*\, L_f^* \qquad \textbf{(26)}$$

Table 1. Dimensionless groups.

$A_1 = \frac{r_d D_f L \quad R_g T}{u_0 R^2 \quad P M_v H}$	residence time / diffusion time
$A_2 = \frac{3}{\phi}$	actual packing solids surface area / characteristic sphere surface area
$A_3 = \frac{K_s H}{C_{g0}}$	biokinetic reaction rate order
$A_4 = \frac{\mu_m X_f \quad R^2 H}{Y \quad r_d D_w C_{g0}}$	maximum growth rate / diffusion rate
$A_5 = \frac{b^0 X_f \quad R^2 H}{Y \quad r_d D_w C_{g0}}$	shear/decay rate / diffusion rate
$A_6 = \epsilon_0$	clean bed porosity
$A_7 = \frac{b_s^0}{b_s^0 + b_d}$	shear rate / total shear/decay rate
$A_8 = \frac{b_d}{b_s^0 + b_d}$	decay rate / total shear/decay rate

Numerical Solution

Equation (16) is solved using an Adams-Moulton finite difference scheme. The solution is found by marching axially through the biofilter. At each axial step, the flux, biofilm concentration profile, biofilm thickness, and packed bed characteristics are evaluated. Equation (15) is solved with a second order two-point boundary value problem direct method. Two levels of iteration are required in each axial step, to handle the non linear term of equation (15), and to calculate the biofilm thickness given by the linearization of equation (21).

The thickness of the biofilm has a physical limit when the bed is clogged. Close to clogging, the assumption of spherical packing solids with a shell of biofilm is not valid. Thus, a minimum bed porosity is defined, that gives a maximum biofilm thickness:

$$L_{f\,max}^* = \frac{A_6 - \epsilon_{min}}{A_2(1 - A_6)} \qquad \textbf{(27)}$$

Experimental Design

The mathematical model and its numerical solution have been derived in a general manner, so they can be applied to any VOC and any trickle-bed air biofilter. The biofilter system used to validate the theoretical work consists of four 15 cm diameter stainless steel reactors, packed with pelletized biological support media (6 mm R-635 Celite) to a depth of 122 cm, with a free board of 91.5 cm. The pelletized medium was selected after initial screening revealed it to be superior to two other candidate media (Sorial et al., 1993). The packing solids are represented in the model as equivalent spheres, with a characteristic radius of 3 mm and calculated sphericity of 0.857. The organic feed to the biofilter consists of a neat solution of toluene volatilized in a feed air stream. The initial concentration of toluene is 250 ppmv. Prior to the addition of toluene, the feed air is purified and contains only oxygen and nitrogen. The biofilters are fed 20 L of an aqueous solution of nutrients per day. There are two possible nitrogen sources, nitrate and ammonia. The temperature of the reactors is maintained at 32 °C throughout the biofilter length and the outlet pressure is very close to atmospheric. The empty bed residence time for both biofilters has been one and two minutes in two different sets of experiments. The biofilters were operated in a co-current mode and backwashed once or twice a week. A more detailed description of the experimental system and its performance can be found in Smith et al. (1994) and Sorial et al. (1995). Table 2 summarizes the values of the system operational variables, biofilter size, packing media, operating conditions and VOC properties. There are two values for the gas flow rate. The first value given in the table is for two minutes residence time and the second value for one minute. The units of the parameters are the ones used in the equation and in the program.

The value of the kinetic and shear parameters (Monod constant, yield coefficient, maximum specific growth rate, decay coefficient, default shear coefficient and biomass density in the biofilm), the biofilm/water diffusivity ratio, and the initial biofilm thickness are not known a priori and cannot be measured in this system, so they are estimated simultaneously with the validation of the model. Assuming that the unknown parameters depend on the nitrogen source, two groups of estimates are calculated, group A and B for the biofilters using nitrate and ammonia respectively.

Table 2. System Parameters.

Packing media parameters		Operating parameters		Biofilter size	
R	0.3 cm	T	305.35 K	L	121.92 cm
ϕ	0.857	P	1 atm	A_T	167.23 cm^2
ϵ_0	0.34	C_{g0}	250 ppmv	VOC properties	
ϵ_{min}	0.025	Q_g	169.93 cm^3/sec 339.86 cm^3/sec		
				D_w	10.8 10^{-6} cm^2/sec
				H	104.03 ppmv/(mg/L)
				M_v	92.13 g/mol

The experimental data used in the validation of the model are:

- The performance of the biofilter with depth, which is obtained from measurements of the substrate concentration in the bulk gas phase for different depths. Data were collected from experiments where the residence time was maintained at one and two minutes. The VOC concentration was measured immediately and two days after the backwashing of the biofilter.

- The biomass concentration profile along the biofilter. This concentration profile was determined at the end of the experimental run. Samples of the media were collected at different depth and analyzed for VSS content. The concentration determined is mass of organic matter per unit volume of biofilter. Two sets of values for each biofilter were available: the biomass concentration immediately after backwashing, and the biomass concentration nine or seven days after backwashing, depending on the biofilter. The residence time was one minute in this experiment.

RESULTS AND DISCUSSION

The study of the mathematical model was carried out in two stages, estimation of the parameters and validation of the model. The validation process involves the test of the accuracy of the model predictions when the estimated values were used. Therefore, two different sets of data were required. Four biofilters were available for this study and two series of experiments were conducted. Initially, three biofilters were running, two using ammonia and one using nitrate as the nitrogen source, and afterwards, the four biofilters were restarted with nitrate. For the first part of the analysis, the estimation of the parameters, the experimental data collected from two biofilters of the first series of experiments were used, each with a different nitrogen source, nitrate in biofilter A, and ammonia in biofilter B. The model was then tested for the two groups of calculated parameters, group A for biofilters using nitrate, and group B, for biofilters using ammonia as a nitrogen source. Data from the four biofilters of the second series of experiments were compared with the model predictions with the parameters of group A (nitrate). The four biofilters were operating at diffrent detention time and initial VOC concentration. The data used to validate the parameters of group B were collected from the other biofilter using ammonia in the first series of experiments. These two different sets of data will be referred to as estimation data set and validation data set in the discussion that follows.

The data of the estimation data set were non-homogeneous: For each biofilter there were two types of observations, removal efficiency and biomass density. Measurements were taken at different sampling points along the reactor depth, and the value of the variable in each point is considered an observation that can be predicted by the mathematical model. Observations are assumed to be independent random variables. Efficiency was measured at four points in biofilter A, and five points in biofilter B. Biomass density was measured at five points in both reactors. The data were taken when both biofilters were considered to be at steady state. For each experiment the initial time, (time=0), is defined as the time immediately after the backwashing of the biofilter. The backwashing technique was practically the same during the realization of all the experiments in the first series, so the state of the system depends only on the time elapsed since backwashing, and therefore, experiments can be replicated.

Two experiments for efficiency measurements were conducted, at one and two minutes detention time. Each experiment was replicated a different number of times, eight replications for one minute detention time and eleven for two minutes. As the reactor

efficiency at each sampling port is assumed to be a random variable, its mean and variance can be calculated as those of the sample generated with the set of replications. In each experiment, the efficiency was measured immediately and two days after backwashing. The value of the initial efficiency has not been used in the validation of the model, because the quasi-steady state derivation of the model is not enough to explain the variation of contaminant concentration profiles with time. As a consequence, the number of model variables corresponding to efficiency observations is eight for biofilter A and ten for biofilter B, (twice the number of sampling ports in the reactor, for one and two minutes detention time).

Two sets of biomass concentration values were available: the initial concentration, and the concentration after nine or seven days, depending on the reactor. There was only one set of measurements for those variables, but as the initial concentration is assumed to be constant along the reactor, we can presume that the five measurements along the bed are realizations of the same random variable, the initial concentration, and therefore, we can calculate the mean and the variance of the variable. For the concentration measurements after nine or seven days there was only one replication, so this value was taken as the mean, and the variance was calculated from the other one adjusted to account for the difference in the number of observations.

Seven unknown parameters were estimated: the yield coefficient Y, that can have values from 0 to 1; the biofilm/water diffusivity ratio, rd, with values from 0 to 1; the maximum growth rate, μ_m; the Monod constant, Ks; the biofilm biomass density, X_f; the initial biofilm thickness, L_{f0}; and the default shear rate and the decay rate coefficients, which were assumed to be equal, and were represented as b_0. To solve the nonlinear parameter estimation problem the method of maximum likelihood was used. The mathematical model can be expressed as:

$$y = f(x) + e$$
$$y = [y_1,...,y_m],\quad f = [f_1,...,f_m],\quad x = [x_1,...,x_n],\quad e = [e_1,...,e_m]. \tag{28}$$

where y is the vector of the m observed variables, e is the residual vector, f is the vector of the model predicted values, and x is the vector of the n parameters. Assuming independent and normally distributed errors, the maximum likelihood parameter estimate, x^*, is the one that minimizes the objective function given by:

$$\phi(x) = \sum_{i=1}^{14} \frac{e_i^2}{\sigma_i^2} = \sum_{i=1}^{14} \frac{(y_i - f_i(x))^2}{\sigma_i^2} \tag{29}$$

where σ_i, is the standard deviation of the ith residual, e_i, the same as the one of the ith observation, y. This is equivalent to the weighted least squares method, with the inverse of the variances as weights. Some prior information, for example, preferred values for the parameters similar to the published ones, was not included in the objective function.

The estimation process was done after a parameter sensitivity analysis. The problem was ill-posed, so conventional methods were not very efficient. The diffusivity ratio, r_d, couldn't be accurately estimated, because the other unknown parameters could be adjusted to get the same reactor response when the value of r_d was modified. Therefore, a typical value was chosen, r_d=0.85. For each value of X_f there was an optimum value of the initial biofilm thickness, L_{f0}, which was calculated from the initial biomass concentration in the reactor that only depends on these two variables, (X_f, L_{f0}). When these three magnitudes were fixed (r_d, X_f, L_{f0}), the number of parameters was reduced to four. Then the reduced problem was solved for different values of X_f and r_d, until the optimum combination was found. It should be noted that when K_s was also fixed, the objective function had a very well-determined minimum, and the optimum estimates for the three remaining parameters (μ_m, Y, b_o) were well-defined. The problem was solved with an iterative technique based on this information, using the estimation data set described before.

The resulting estimated parameters are presented in Table 3 for both biofilters, and the observed and predicted values of the model variables are in Figure 2 for biofilter A and in Figure 3 for biofilter B. The error bars shown in the removal efficiency graphs correspond to the 95% confidence value for the mean. The values are plotted against the relative reactor depth, that is, the depth divided by the total length of the reactor, L. The value of z is the axial coordinate, so $z=0$, corresponds to the inlet of the reactor. Although the optimum parameter values for biofilter B are those of set number 1, in Figure 3 the results corresponding to a different set of parameters, set number 2, are shown. The values are given also in Table 3. The reason to consider this new set is that the fit for the efficiency observations is much better. The fit for the biomass is worse, though. We have more confidence in the efficiency observations because there are various replications of the experiment, and, on the other hand, the measurements of biomass can be inaccurate, due to the presence of inactive biomass that is not included in the model. It is possible then, to prefer parameter set 2 as the optimum, although the objective function does not reach a minimum in this point. This arises the problem of defining an objective

Table 3. Biofilter parameter estimates.

	Xf (mg/L)	L_{f_0} (cm)	K_s (mg VOC/L)	Y (mgVSS/ mg VOC)	r_d	μ_m		b_0	
						sec^{-1}	day^{-1}	sec^{-1}	day^{-1}
Biofilter A	10,000	0.0345	0.5	0.15	0.85	$0.095*10^{-4}$	0.82	$0.12*10^{-7}$	0.001
Biofilter B									
Set 1	10,000	0.041	0.1	0.2	0.85	$0.04*10^{-4}$	0.35	$1.2*10^{-7}$	0.01
Set 2	10,000	0.041	5.0	0.15	0.85	$0.36*10^{-4}$	3.11	$0.12*10^{-7}$	0.001

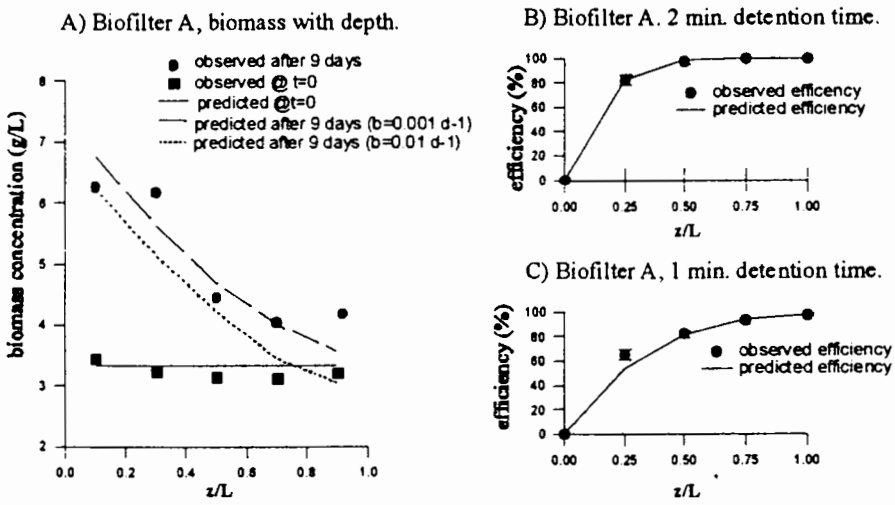

Figure 2. Performance of biofilter A using nitrate as the nitrogen source. A) Biomass concentration in the reactor with depth, the detention time is 1 minute. B) and C) Removal efficiency with depth, the detention time is 2 minutes in B) and 1 minute in C).

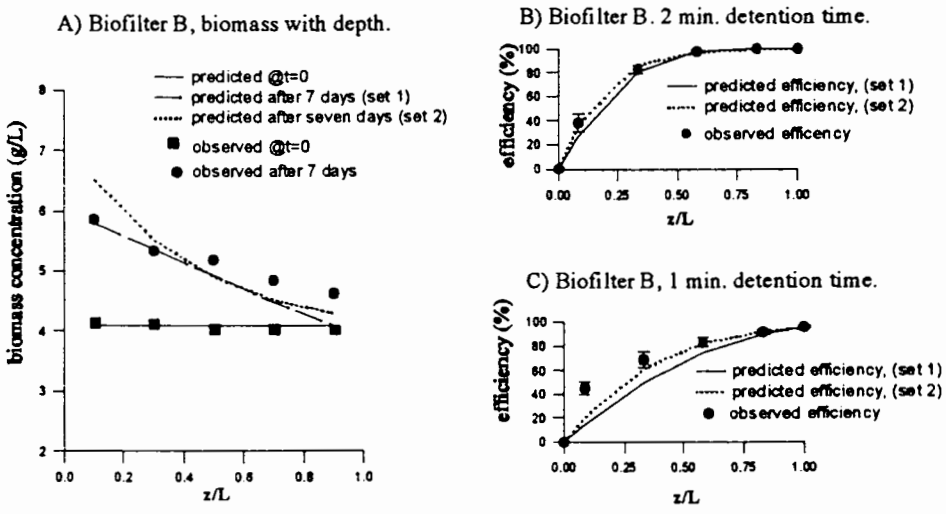

Figure 3. Performance of biofilter B using ammonia as the nitrogen source. A) Biomass concentration in the reactor with depth, the detention time is 1 minute. B) and C) Removal efficiency with depth, the detention time is 2 minutes in B) and 1 minute in C).

function that would include all the prior information. Here the solution is considered non-unique, and more objective information is needed to select a set. When the model is used for prediction, set 1 gives slightly better results. This problem was not found in biofilter A, but although the optimum value is b_0=0.12 *10^{-7} sec^{-1}, another value of b_0 is considered for comparison.

Overall, the model is close to the observed values. The fit is much better for the removal efficiency than for the biomass reactor concentration, although the efficiency in the points closer to the reactor inlet is consistently underpredicted. The overall predicted efficiency is very close to the observed value, in fact, this is the point with less variability in the measurements. The initial biomass is also very close, but not the rest of biomass values.

Most of the parameters found are in the typical range. Arcangeli and Arvin (1992) reported a set of kinetic parameters for toluene degradation in a bioreactor: r_d=0.9; K_s=0.6 mg COD/L=0.19 mgVOC /L, and X_f=12000 mg/L. The rest of the kinetics values in the mentioned paper are referred to the two bacterial species considered in their model, so they are not compared with the ones here. Ottengraf (1986a) calculated the maximum growth rate for toluene degradation as: μ_m=0.6d^{-1}. All these values are in good agreement with the ones computed here. The value of b_0

is too low, because typically it is reported to be around 0.1d^{-1}. In Figure 2, the biomass concentration profile is shown for two values of b_0, the optimal value and b_0=0.01 d^{-1}, with the rest of the parameters unchanged. The concentration profile is the same for both values. It can be seen that the profile has the same shape but the magnitudes are lower, and the fit is worse. This is another reason to prefer parameter set 1 in biofilter B, because the value of the decay coefficient is higher. One possible explanation for this low shear and decay rate can be that we are considering all biomass as active, when it is not, so the model should be modified to account for non-homogeneous biomass. In fact, the model assume that the inactive biomass produced by decay is lost, and this may not be true. The observed net yield coefficient calculated from experimental data, the VSS lost and removed with backwashing and the amount of toluene consumed, is 0.23 mg VSS/ mg TOL for biofilter A, and 0.27 mg VSS/ mg TOL for biofilter B. This values are close to the estimated yield coefficients.

The model was tested in the prediction of the removal efficiency of biofilters fed with nitrate and ammonia, operating at different conditions. As mentioned before, the validation data set was used. The new set of observations contains six subsets of data. Four of them will be compared with the model predictions with parameter group A (nitrate), and the last two ones with the model predictions with parameter group B (ammonia). The results and the conditions of operation for biofilters using nitrate are in Figure 4, and for biofilters using ammonia in Figure 5. The detention time of the reactor, θ, and the initial VOC concentration in the gas phase, C_{g0}, were the parameters varied. Measurements were conducted for different backwashing techniques in the four biofilters using nitrate. This process is not included in the mathematical model but it is presumed that it will have an effect in the biofilter performance because the removal efficiency differs with the backwashing technique. A description of this system can be found in Sorial et al (1995). Two sets of measurements are presented for each biofilter in Figure 4, and it can be seen that the best fit does not corresponds to the same backwashing technique in all of them. This suggests the need of including the backwashing process in the model. The prediction for the biofilter using ammonia has been done with parameter set 1, and the fit is reasonably good. The backwashing technique was not varied in the experiments with ammonia.

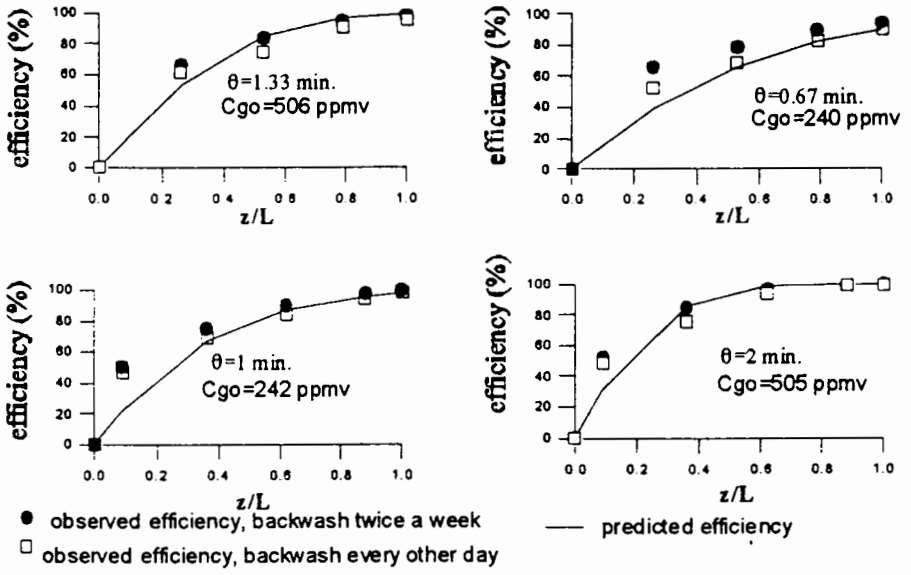

Figure 4. Predicted and observed removal efficiency values for biofilters using nitrate as the nitrogen source.

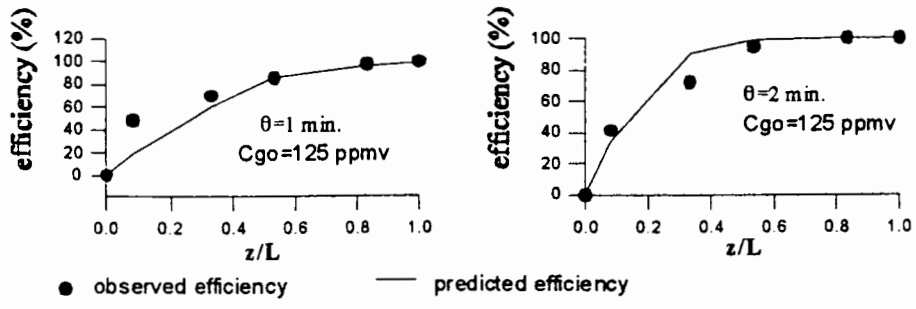

Figure 5. Predicted and observed removal effciency values for a biofilter using ammonia as the nitrogen source.

CONCLUSIONS

A mathematical model to describe the biodegradation of a waste gas in a trickle-bed reactor has been proposed and validated. The model considers a two phase system, one limiting substrate and quasi-steady state. In the model analysis the unknown reactor parameters have been estimated and the model has been validated. Two sets of observations have been employed. For the estimation of the parameters, the biofilter removal efficiency profiles and the biomass concentration in the reactor have been calculated and compared with experimental data from two different reactors, one using nitrate as a nitrogen source and the other one using ammonia.

These parameters are the kinetic constants: biomass density in the film, Monod constant, maximum growth rate, yield coefficient and decay and shear rate coefficients; and the initial biofilm thickness and the ratio between the VOC diffusivity in the biofilm and water. Once the values of the parameters are known for both systems, the model has been tested in the prediction of the biofilter efficiency for the same type of reactors operating in different conditions. The detention time and the initial VOC concentration were the varied parameters.

The fit of the model is reasonably good for the efficiency values and somewhat worse for the biomass concentration measurements. There is a systematic underprediction of the efficiency observations close to the reactor inlet. The values of the estimated parameters are close to the typical values reported by previous investigators, except for the decay coefficient that is unusually low. The model was tested with different sets of observations of biofilter efficiency profiles, for different scenarios. The results conclude that the model is valid and can be used for prediction with acceptable accuracy, especially in the overall biofilter efficiency value.

Some problems in the mathematical model have been identified. First, it cannot predict the variation of the contaminant concentration profiles with time, a dynamic model is necessary, it has to account for time variations in the concentration and in the biomass distribution. Second, the prediction of the biomass concentration is not very good, nonhomogeneous biomass, active and inactive microorganisms, should be considered. The calculated decay rate coefficient is very low, this value should be verified with a more accurate model or with more observations. Some operational parameters should be included in the model, as oxygen and nutrient limitations, and backwashing technique effects. This will be done in future work.

There are also problems in the parameter estimation technique. The objective function does not include all the prior information and thus, the selection of the optimum parameter set is subjective in some cases. Also the problem is ill-posed and conventional algorithms do not give good results. A careful study of the problem is needed to determine what parameters can be accurately estimate, what is the most suitable method to approach this problem and what kind of experiments should be carried to obtain the more valuable information.

APPENDIX

Notation

a_0 (cm^{-1}), surface area per unit volume
a_f (cm^{-1}), surface area per unit volume accounting for biofilm in bed
A_1-A_8, dimensionless groups
b (sec^{-1}), shear/decay rate coefficient
b^0 (sec^{-1}), default shear/decay rate coefficient
b_d (sec^{-1}), decay rate coefficient
b_0 (sec^{-1}), decay and shear rate coefficient for the parameter estimation
b_s (sec^{-1}), shear rate coefficient
b^0_s (sec^{-1}), default shear rate coefficient
C_f (mg/L), biofilm VOC concentration
C_g (ppmv), gas phase VOC concentration
C_{g0} (ppmv), inlet gas phase VOC concentration
D_f (cm^2/sec), VOC diffusivity in the biofilm
D_w (cm^2/sec), VOC diffusivity in water
H (ppm/(mg/L)), Henry's law constant
J (ppm cm/sec), VOC flux in gas phase
J_f (mg cm/L sec), VOC flux in biofilm
K_s (mg/L), Monod saturation constant
L (cm), biofilter packing media length
L_f (cm), biofilm thickness
$L_{f\,max}$ (cm), maximum biofilm thickness
M_v (g/mol), VOC molecular weight
r (cm), radial coordinate
rd, ratio between VOC diffusivities in biofilm and water
R (cm), characteristic packing sphere radius
R_g (cm^3 atm/mol K), universal gas constant
t (sec), time

T (K), system temperature
u_0 (cm/sec), approach velocity to the biofilter
X_f (mg/L), biomass density
Y (mg biomass/ mg VOC), yield coefficient
z (cm), axial coordinate

Greek letters
β, stress proportionality constant
ϵ_0, clean bed porosity
ϵ_f, porosity in bed with biofilm
ϵ_{min}, minimum porosity allowed in packed bed
ϕ, sphericity of packing solids
μ_m (sec^{-1}), maximum growth rate
τ ($dyne/cm^2$), shear stress
θ (min), and detention time.

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16. ABSTRACT The objective of this paper is to define and validate a mathematical model that describes the physical and biological processes occurring in a trickle-bed air biofilter for waste gas treatment. The model assumes a two phase system, quasi-steady state and one limiting substrate. Experimental data from the biodegradation of toluene in a pilot system with four packed bed reactors, are used to test the validity of the model. The unknown biofilter variables are estimated using a non-linear paramter estimation technique. Using these parameter values, simulations were carried out for different operational conditions, and the model predictions were compared to experimental data.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
VOC biofiltration	trickle-bed biofilter, mathematical model, waste gas treatment	

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