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Analysis and comparison of biofilter models

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Abstract

Realistic mathematical models are essential for the scaling-up or the design of biofilters. However, the mathematical models which describe the steady-state and the transient operation of biofilters are very limited. Although some of these models are based on restrictive assumptions, they have been widely used in industry for designing actual biofilter units. This study gives detailed analysis and comparison between these models. The asymptotic behavior of recent models are presented. The results show that diffusion is an important phenomenon which should not be neglected in developing biofilter models, and that neglecting oxygen transport and its effects on growth kinetics will give unrealistic values for the effective as well as the actual film thickness.

Keywords: Biofilters; Volatile organic compounds

1. Introduction

An intense effort on reducing VOC (volatile organic compound) emissions has led to the development of biofiltration technology which is an environmentally friendly and costeffective method compared to other alternative technologies, such as incineration, activated carbon adsorption and chemical washing in packed-columns for the treatment of VOC emissions. Biofiltration is a technology based on the biological oxidation of VOCs using micro-organisms which are immobilized forming biofilms or biolayers around solid particles such as peat, compost, and a peat/perlite mixture. These immobilized particles are packed in a column known as a biofilter. The VOC pollutants in the contaminated air that pass through the biofilter, which is also known as a vapor phase bioreactor, are transported into the biofilm by diffusion. The biooxidation reactions take place in the biofilm. If the residence time and the size of the biofilter are large enough then the existing stream will be pollutant-free air which will meet any acceptable regulatory standards, such as the EPA regulations on VOCs. There are three different types of biofilters and the term trickling biofilter or bioscrubber is used in cases where a recirculating water stream flows continuously through the biofilter. Classical biofilters do not have a continuous liquid stream. The required moisture is provided by saturating the airstream before it enters the biofilter, and/or by supplying liquid water occasionally as required. In this

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article, we focus on the models of classical type of biofilters.

A number of experimental studies have demonstrated that the removal of VOCs in biofilters is feasible, e.g. $[1-3]$. However, research into the theoretical studies regarding biofilter models is rather limited. The most widely used model is the work of Ottengraf [I] and Ottengraf and van den Oever [21. This model is based on the following simplifying assumptions: (i) Kinetics: two limiting cases, zero-order [21 and first-order $[1]$ in the nutrient concentration, were considered. Implicitly, oxygen was assumed to be in excess, thus oxygen limitation on kinetics was ignored. (ii) The biofilm thickness (δ^*) was assumed small compared to the diameter of the support particles and a constant value for the film thickness was used throughout the reactor despite the changes in the VOC concentration along the biofilter column. (iii) The transport of the nutrients into the biofilm is by diffusion. (iv) Gas phase is in plug flow. Although this model is based on some rather simplistic assumptions, it has been widely used because of the ease of obtaining analytical expressions from the solution of the model. The simple analytical expressions have been used not only in validating laboratory-scale experimental data but also in the actual design of pilot-scale biofilter units. For example, van Lith et al. [4] developed design criteria based on this model and applied them in designing actual biofilter units at Clair-Tech, the Netherlands. Similarly, Dharmavaram [5] of E.I. Dupont de Nemours $\&$ Co., DE, USA, also reports design criteria based on this model.

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In a recent study, Zarook et al. [3] extended the work of Ottengraf [21 and presented a detailed steady-state biofiltration model for single VOCs. In this model: (i) The actual kinetic expressions resulting from shake-flask experiments were used instead of limiting cases such as zero- or first-order kinetics. (ii) Oxygen was also considered in the growth rate expression, i.e. oxygen was not assumed to be in excess. (iii) The film thickness was not assumed to be constant throughout the column and it was determined as the thickness of the biolayer where one of the limiting substrates (either VOC or oxygen) depletes before it reaches the biolayers/solid support interface. Model equations based on these improvements constituted a two point non-linear boundary value problem for which analytical solutions were not possible. Since both the models of Zarook et al. [3] and Ottengraf [1] and Ottengraf and van den Oever [21 are valid for, steady-state, single VOC removal, a detailed analysis and comparison between these models are necessary and important so that the appropriate model can be used for the experimental validation of the models, and for designing or scaling-up of the biofilter units. The major objective of the present study is to present the results of the analysis and comparison between these models.

Ottengraf and van den Oever [2] have used the single VOC biofiltration model to describe VOC mixture removal in an additive sense. However, recent studies [6,7] have shown that the degradation kinetics of mixed VOCs may be significantly different. Baltizis and Zarook [6] have extended their model to describe the biofiltration of VOC mixtures under steady-state conditions. In their work, they took into account competitive inhibition kinetics.

Biofiltration is a technology for treating VOC emissions. The emission level is unlikely to be constant, thus biofilters are more likely to operate under unsteady-state conditions. However, theoretical studies on the transient performance of biofilters are scarce. Deshusses and Dunn [7] reports a transient biofiltration model which is based on the assumption that oxygen is in excess and the kinetics are of the Michaelis-Menten or Monod type. For the VOCs considered, they experimentally verified this assumption to be valid. Thus, this model can be used only if oxygen is not limiting the process. Recently, the steady-state model of Zarook et al. [3] was extended to describe the transient performance [8] of the biofilters. This model took into account the adsorption phenomena as well as the reaction and mass transfer of both the oxygen and VOC. While all the steady-state and transient biofiltration models $[1-3,6-8]$ are based on the assumption that substrates are transported into the biofilm through diffusion, the very recent transient model of Hodge and Devinny [9] treats the biofilm and the solid as a single phase, thus diffusion in the biofilm and details of the adsorption process are ignored. Furthermore, this model is also based on the assumption of first-order kinetics for biodegradation rate and of excess oxygen. Asymptotic behavior studies and a comparison between several model discussed above are also presented in this work.

2. Theory and analysis

A steady-state biofiltration model constitutes a set of mass balances within the biofilm as shown in Fig. 1 and in the gas phase. The assumptions on which the model equations are based are given in detail elsewhere [3,6]. Here, for comparison purposes, we present the model equations for removal of a single VOC. The mass balance equations in the biofilm are :

$$
D\frac{d^2C_1}{dx^2} = \frac{X_V}{Y}\,\mu(C_1, C_{10})\tag{1}
$$

$$
D_{\rm O} \frac{d^2 C_{\rm IO}}{dx^2} = \frac{X_{\rm V}}{Y_{\rm O}} \mu(C_{\rm I}, C_{\rm IO}) \tag{2}
$$

with boundary conditions:

$$
C_1 = \frac{C_g}{m} \text{ and } C_{10} = \frac{C_{g0}}{m_O} \text{ at } x = 0
$$
 (3)

$$
\frac{dC_1}{dx} = 0 \text{ and } \frac{dC_{10}}{dx} = 0 \text{ at } x = \delta \tag{4}
$$

For biological systems, specific growth rate, μ , has the form of either Monod-type kinetic dependence as given in Eq. (5) or Andrews-type kinetic dependence as in Eq. (6), below.

Monod kinetics:

$$
\mu = \frac{\mu_{\rm m} C_1}{K + C_1} \tag{5}
$$

Andrews kinetics:

$$
\mu = \frac{\mu^* C_1}{K + C_1 + \frac{C_1^2}{K_1}}
$$
\n(6)

When oxygen also limits the biodegradation rate, then the specific growth rate is given by an interactive model. In this case Eqs. (5) and (6) need to be modified as follows. Interactive model from Monod kinetics:

$$
\mu = \frac{\mu_{\rm m} C_1}{K + C_1} \left[\frac{C_{\rm 1O}}{K_0 + C_{\rm 1O}} \right] \tag{7}
$$

Interactive model from Andrews kinetics:

$$
\mu = \frac{\mu^* C_1}{K + C_1 + \frac{C_1^2}{K_1}} \left[\frac{C_{10}}{K_0 + C_{10}} \right]
$$
 (8)

Along the biofilter column, mass balances in the gas phase are:

$$
u_{g} \frac{dC_{g}}{dh} = A_{S} D \left[\frac{dC_{1}}{dx} \right]_{x=0} \tag{9}
$$

$$
u_{\rm g} \frac{dC_{\rm gO}}{dh} = A_{\rm S} D_{\rm O} \left[\frac{dC_{\rm IO}}{dx} \right]_{x=0} \tag{10}
$$

with initial conditions

$$
C_{\rm g} = C_{\rm gi} \text{ and } C_{\rm gO} = C_{\rm gOi} \text{ at } h = 0 \tag{11}
$$

2.1 Asymptotic behavior of the model

Ottengraf and van den Oever [2] implicitly assume that oxygen is in excess and it does not exert any limitation on the biodegradation rate. In general, the biodegradation rate in the biofilm can be expressed as

$$
-r = \frac{X_V}{Y} \mu \tag{12}
$$

Although the authors $[2]$ acknowledge that based on shakeflask experiments the biodegradation kinetics of single VOCs follow the Monod model $(Eq. (5))$, they only consider two limiting cases. At high concentrations they assume zero-order kinetics while at low concentration they assume first-order kinetics. Thus, in the excess oxygen limitation ($C_{10} \gg K_0$) for a large value of C_{10} , Eq. (7) gives a zero-order reaction rate as,

$$
-r = \left(\frac{X_V}{Y} \mu_m\right) = k_0 \qquad (C_1 \gg K) \tag{13}
$$

Similarly, a first-order reaction rate is given by

$$
-r = \left(\frac{X_{\rm V}}{Y}\frac{\mu_{\rm m}}{K}\right)C_1 = k_1C_1 \qquad (C_1 \ll K) \tag{14}
$$

Hence, for zero- and first-order kinetics, under no oxygen limitation, the biofilm side model equations are given as $[1,2]$:

$$
D\frac{d^2C_1}{dx^2} = k_0 \tag{15}
$$

$$
D\frac{d^2C_1}{dx^2} = k_1C_1
$$
 (16)

Since oxygen was assumed to be in excess, boundary conditions 3 and 4, involving C_{1Q} and C_{gQ} will not be necessary. Similarly, under this condition, one needs only Eqs. (9) and (11) $(C_g = C_{gi}$ at $h = 0$) for the gas phase side. Thus, the model equations of Zarook et al. [3] asymptotically reduce to the model of Ottengraf [1] and Ottengraf and van den Oever [2].

2.2. Limiting cases

2.2. I. Zero-order kinetics (diffusion limitation and reaction limitation)

When the biodegradation rate is assumed to be zero-order, one can clearly identify two regimes of operation: diffusion limited and reaction limited regimes. In the diffusion limited regime, the rate of diffusion is slow compared to the VOC utilization rate in the biofilm [21. Ottengraf and van den Oever $[2]$ showed that the *effective biofilm thickness* for this region is given by

$$
\delta = \sqrt{\frac{2DC_{\rm g}}{k_0 m}}
$$
 (17)

Here, one should be aware that equation 17 is based on the assumption that the VOC gets completely consumed in a portion of the actual biofilm thickness. However, if oxygen is limiting then the effective biofilm thickness calculated using Eq. (17) may be invalid. The concentration profile along the biofilter for zero-order kinetics for the diffusion limited regime is given by [21

$$
\frac{C_{\rm g}}{C_{\rm gi}} = \left\{ 1 - \frac{A_{\rm S}h}{u_{\rm g}} \sqrt{\frac{k_0 D}{2m C_{\rm gi}}} \right\}^2 \tag{18}
$$

In the reaction limited regime, the total biofilm is fully active. For this case, the concentration profile in the gas phase is given by $[2]$

$$
\frac{C_{\rm g}}{C_{\rm gi}} = 1 - \frac{A_{\rm s} \delta^* h k_0}{C_{\rm gi} u_{\rm g}} \tag{19}
$$

where δ^* is the actual biofilm thickness.

2.2.2. First-order kinetics

If the degradation rate is assumed to be first-order, one can not clearly distinguish between reaction and diffusion limited regimes as in the zero-order case. This can be easily shown from the concentration profiles in the biofilm [11. For the first-order case, the gas phase concentration profile is given by

$$
\frac{C_{\rm g}}{C_{\rm gi}} = \exp\bigg\{-\frac{hA_{\rm s}D\phi\tan\phi}{\delta^*m u_{\rm g}}\bigg\} \tag{20}
$$

where ϕ is known as Thiele modulus [1,3] which is defined as:

$$
\phi = \delta^* \sqrt{\frac{k_1}{D}} \tag{21}
$$

Thiele modulus represents the ratio of biodegradation rate to diffusion rate. From the value of the Thiele modulus one may be able to distinguish the regimes of operation.

3. Results and discussion

For analysis and comparison of the models of Ottengraf [1] and Ottengraf and van den Oever [2] against the model of Zarook et al. [31, steady-state experimental biofiltration data published earlier [3] can be used. Analytical solutions to the model (Eqs. (1) - (11)) is not possible, hence the model equations have been solved numerically. Parameters needed to solve the model equations were more realistically estimated and details of the methods and the solution procedure were given elsewhere [3]. It should be mentioned that except for the parameter $A_{\rm S}$, all other parameters were found experimentally or from the literature. The parameter A_s was found as the value which minimized the sum of the squares of the error between the experimental and the model predicted concentrations. This value was unchanged and used to predict the other experimental data. The first four entries of Table 1 were used for finding the parameter A_S and the last three entries were used for predicting. In columns 2, 3 and 4 of Table 1, superficial velocity, inlet concentration and volume of packing are given, respectively. Results are given in terms of the experimental and model predicted removal rates (column 5 and 6). Percentage error (E) is based on the experimental values and it is given in column 7. Removal rate, also known as elimination capacity, is defined as the amount of VOC removed (gram) per volume $(m³)$ of packing material per time (h) . For the model of Zarook et al. $[3]$, percentage error (E) between the model predicted and experimentally evaluated removal rates is given in column 7. Furthermore, all the percentage errors (E, E_{DL} , E_{RL} and E_{first}) reported in Table 1 are calculated in relation to the experimental values given in column 5. Details of the experimental procedure were reported elsewhere [3]. The model predicted concentration profiles along the biofilter column as well as the removal rates were in excellent agreement with the experimental data [3]. Furthermore, the results also showed that the effective film thickness estimated did not exceed $110 \mu m$.

Following the same procedure as discussed in $[3]$, we have estimated the biolayer surface area, A_s , through Eq. (18) in combination with Eq. (13) for the case of zero-order kinetics in the diffusion limited regimes. This parameter was found to be $246.8 \text{ m}^2 \text{ m}^{-3}$. However, Zarook et al. [3] report a value of $85.15 \text{ m}^2 \text{ m}^{-3}$. Thus, the zero-order (diffusion limited) model predicts a three times larger value. Furthermore, the effective film thickness estimated through Eq. (17) ranges from 1700–8800 μ m. It should be mentioned that the particle size used in the experiments $\lceil 3 \rceil$ averages about 4000 μ m. Thus, the assumption of planner geometry for biofilm side is questionable, if one assumes zero-order kinetics instead of actual kinetics. The film thickness evaluated through Eq. (17) is based on the depletion of VOC only. If oxygen is also assumed to be a limiting compound, then a more realistic value for the film thickness would have been obtained. Fig. 2 shows the concentration profiles in the biofilm as predicted by Zarook et al. [3]. In this case, one can see that it is oxygen that determines the value of δ and not the VOC. In columns 8 and 9 of Table 1, the removal rates

 \circ \sim

Fig. 2. Concentration profiles of oxygen and VOC in the biofilm at a patticular location in the biofilter.

 $(R_{zero-DL})$ and percentage errors (E_{DL}) calculated based on the zero-order (diffusion limited) model are given, respectively. The percentage errors of this model given in column 9 are larger compared to the percentage errors given in column 7. The removal rate is calculated based on the inlet and exit concentrations. In Fig. 3, the intermediate as well as the exit concentrations predicted by both models are compared against the experimental values. In this case, the prediction by the zero-order model is not in good agreement as compared to the model of Zarook et al. [31.

For the case of zero-order kinetics under a reaction limited regime, as seen from Eq. (19), we need to estimate A_s (biolayer surface area per reactor volume) and δ^* (actual film thickness). The actual film thickness is very difficult to estimate or measure experimentally and it varies along the biofilter. Hence for this case, the combined parameter $(A_s \delta^*)$ is fitted to the first four data sets. Once the value was determined, then the same parameter was used to predict the other sets. The combined parameter was found to be 1.52. If one uses a value 85.15 or 246.8 m² m⁻³ for A_s, then δ^* will be 6 or 18 mm, respectively. For an actual film thickness, these

Fig. 3. Comparison of biofilter models with the experimental data.

values are very large and unrealistic. Also this model is based on the assumption of a constant film thickness along the biofilter. Furthermore, from Eq. (19), one can easily show that the removal rate is given by $A_s \delta^* k_0$. Thus, despite the changes in the inlet concentration and flow rates, one gets constant removal rates $(R_{zero-RL})$ as shown in column 10 of Table 1. The maximum percentage difference (E_{RL}) in column 11) is as high as 67.7%.

When the kinetics are assumed to be first-order, then one can not clearly distinguish between different regimes. For this case, an analytical solution was possible and it is given in Eq. (20). The first-order reaction rate constant was estimated through Eq. (14). As in the previous case, we have two parameters A_s and δ^* which need to be found. However, as seen from Eq. (20), here we can not lump $(A_S \delta[*])$ simply as in the previous case. In order to find this parameter, Eq. (20) is expanded using the Taylor series as follows

$$
\frac{C_{\rm g}}{C_{\rm gi}} = \exp\bigg\{-\frac{h}{mu_{\rm g}}\bigg(A_{\rm S}\delta^*k_1 + \frac{A_{\rm S}\delta^{*3}k_1}{3D} + \frac{A_{\rm S}\delta^{*5}k_1}{3D^2} + ...\bigg\}\bigg\}
$$
\n(22)

When neglecting higher order terms one can write Eq. (22) as

$$
\frac{C_{\rm g}}{C_{\rm gi}} = \exp\bigg\{-\frac{hA_s\delta^*k_1}{mu_{\rm g}}\bigg\} \tag{23}
$$

Now as in the previous case, $(A_s \delta^*)$ was found by fitting to four sets of data. The value was found to be 0.38 which is exactly l/4 of the value that we found for the case of zeroorder kinetics. Thus, the actual film thickness (δ^*) was found to be 1.5 or 4.5 mm depending on the value used for A_s . Although the lower value for A_s seems to be reasonable, the removal rates (R_{first}) calculated using this model (given in column 12) show that in almost all cases, the agreement with the experimental data is poor. This can be easily seen from the percentage errors (E_{first}) given in column 13.

A direct comparison of the model of Hodge and Devinny [91 is not possible as they ignore the diffusion phenomenon in the biofilm. The ratio of $[A_s \delta^* m]$ in Eq. (23) can be easily written as $[A_S \delta^* C_1 C_g]$ which is the ratio of mass of VOC in the biofilm to the mass of VOC in the air. A symbol k_m is given for this term in Hodge and Devinny's [91 work. Thus, it is interesting to note that in the limit, their model and the model of Ottengraf [1] for the case of first-order kinetics are identical. When neglecting higher order terms in Eq. (22), the diffusivity terms get canceled out, thus the diffusion phenomenon is ignored. It is needless to state that the results of the comparison that we made for the case of first-order model of Ottengraf [1 J is also valid for this case. A more elaborate analysis can be made through the notion of Thiele modulus and the effectiveness factor which is defined as the ratio of actual rate of reaction to the rate of reaction that would result

Fig. 4. Effectiveness factor versus Thiele modulus along the biofilter column. Curves 1, 2, 3 and 4 are for first four sets of data given in Table 1.

if the entire biofilm was exposed to the concentration at the gas/biofilm interface. Zarook et al. [3] and Zarook and Baltzis [81 define the Thiele modulus as

$$
\phi = \delta \sqrt{\frac{\mu^* X_V}{KDY}} \tag{24}
$$

and effectiveness factor as

$$
\eta = \frac{-D\left(\frac{dC_1}{dx}\right)_{x=0}}{\frac{\delta X_V}{Y} \left[(C_1, C_{10}) \right]_{x=0}}
$$
(25)

Model Eqs. (1) - (4) related to mass balances in the biofilm. and Eq. $(9)-(11)$ related to the mass balances in the gas phase along with the growth rate expression (Eq. (S)) have been solved numerically. The effectiveness factor and Thiele modulus are found using Eqs. (24) and (25), respectively. The effectiveness factor versus Thiele modulus along the column are plotted on a log-log scale as shown in Fig. 4. Curves 1, 2, 3 and 4 are for the first 4 sets of data given in Table 1. Fig. 4 shows that when Thiele modulus is large $(\phi > 5)$, the effectiveness factor η can be as low as 0.15. Thus, a low value for η implies that the rate of diffusion is slow as compared to the biodegradation rate, and diffusion may control the overall process. The same observation was found for experimental data sets 5 and 6 of Table 1. However, for data set 7, the effectiveness factor along the bed increased to a value of 1.7 at the exit of the biofilter column as shown in Fig. 5. Since the biofilm thickness (δ) varies along the biofilter column, due to consumption of VOC of oxygen, the Thiele modulus and the effectiveness factor will vary with δ for the same inlet concentration of VOC to the biofilter. Thus, from the inlet to the exit of the biofilter, the overall process may vary from diffusion control to reaction control regimes or vice versa. The results clearly show that diffusion is an important phenomenon in the biofiltration process which should not be neglected.

Fig. 5 Effectiveness factor versus dimensionless height along the biofilter column. The curve is for the data set 7 given in Table 1.

4. Conclusion

In this work, models of Ottengraf [l] and Ottengraf and van den Oever [21 have been compared against the model of Zarook et al. [3]. The results indicate that the effective film thickness calculated for zero-order kinetics under diffusion limited regimes is larger than the particle size used. This large value contradicts the assumption of planner geometry. Similarly, the zero-order reaction limited model predicts unrealistically large values for the actual film thickness and that the removal rates calculated from it are the same for all the seven sets of data. This is not in agreement with the experimental data. The first-order reaction kinetic model shows the highest percentage deviation between the model predicted and the experimentally found removal rates. The results also show that one can not simply assume that oxygen is in excess, thus the transport of oxygen as well as its limitation on growth kinetics should be considered so that meaningful results can be obtained.

The effectiveness factor calculations have shown that diffusion is a very important phenomenon which should not be neglected when modeling the biofiltration process. It is also shown that the limit the Zarook et al.'s model $[3]$ asymptotically reaches all other models when oxygen is assumed to be in excess, kinetics are of simple type and of constant film thickness. In summary, careful consideration should be given to the choice of the biofilter model and the assumptions on which these biofilter models are based for the purpose of validating experimental data or designing or scaling-up of biofilters.

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Appendix A: Nomenclature

gen consumed

Greek letters

Subscripts

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