Simplified and Monod kinetics in one-dimensional biofilm reactor modelling: a comparison

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Abstract A theoretical study supported by some experimental tests has been carried out with the aim of comparing one-dimensional (1-D) biofilm reactor models that use simplified (zero- and first-order) and Monod kinetics. Two different situations have been compared: one rate-limiting substrate with or without liquid film diffusion. The results obtained show that the use of a simplified kinetic approach compared to the Monod kinetic approach determines (1) an unjustified overestimate of the removal rate, especially for thin biofilms, and (2) an excessive overestimate of the liquid film layer thickness necessary to justify high kinetic orders. Even if recent research projects show that biofilm structure is more complicated than the one assumed in the modelling approach used in this study, nevertheless 1-D models still now continue to be the only ones that can reasonably support process engineers in biofilm reactor design, due to their intrinsic simplicity and the need for small sets of input data and parameters that can be obtained theoretically or often empirically.

Keywords Biofilm reactors; liquid film diffusion; modelling; Monod kinetic; one-dimensional (1-D) models; simplified (fixed-order) kinetics

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Introduction

Biofilms are ubiquitous and can occur in nature on almost any surface that is in contact with water. Biofilm reactors are used beneficially for the treatment of water and wastewater and in bioremediation of groundwater and soil.

A great interest in biofilm reactors/systems has been demonstrated by the large number of international specialised conferences, symposia and workshops organised in the last 10 years by the International Association on Water Pollution Research and Control (IAWPRC)-International Association on Water Quality (IAWQ) whose selected proceedings have been published as issues of the journal *Water Science & Technology* (Bernard, 1990; Pujol, 1994; Rogalla and Harremoës, 1994; Arvin, 1995; van Loosdrecht and Tijhuis, 1995; Harremoës, 1997; The Conference Program Committee, 1998; Rittmann, 1999).

The results of the research projects carried out in the 1990s show that:

- biofilm structure is not homogeneous either physically or biologically (Bishop and Rittmann, 1995);
- hydrodynamic characteristics like flow velocity, flow regime (laminar/turbulent) and shear stress are important factors influencing mass transfer, detachment rate and, definitely, structure of the biofilm (Gjaltema and Grieb, 1995; Wilderer *et al.*, 1995);
- adsorption, transport, hydrolysis, predation are examples of the important effects of organic and inorganic solids, together with population dynamics and hydrodynamics, on the behaviour of biofilm systems (Nielsen and Harremoës, 1995).

The mathematical description of biofilm systems taking into account complex biofilm structure, population dynamics and hydrodynamic effects needs the use of 3-D models. Different 3-D models have been recently developed (*inter alia*, Picioreanu *et al.*, 1999; Rittmann *et al.*, 1999). These models are able efficiently to describe the outcome of a biofim process for which the biofilm structure (pores/channels, cell clusters and flow pattern) is known or to predict the biofilm structure and its functions as output of the model,

but they need particular sets of input data and parameters not always easily available for process engineers involved in the design of biofilm reactors on the basis of conventional design data (flow-rate and pollutants loadings).

One-dimensional (1-D) models describe biofilms as uniform steady-state films containing a single type of organism and governed exclusively by 1-D mass transport and biochemical transformations (*inter alia*, Harremoës, 1978; Rittmann and Dovantzis, 1983), even if stratified steady-state and dynamic models able to represent multi-substrate, multi-species biofilms have also been developed (*inter alia*, Wanner and Gujer, 1984). These models generally represent a simple description of the behaviour of biofilms, but are characterised by the need of small sets of input data and parameters that can be obtained theoretically or often empirically.

Although simplifications and assumptions used in 1-D models are often not able to completely describe recent experimental observations (Noguera *et al.*, 1999) and this suggests the use of more realistic approaches for advanced biofilm research purposes, they still now continue to be the only ones that can reasonably support process engineers in biofilm reactor design, due to their intrinsic simplicity. In fact, these potential user are interested only in a gross output (e.g. a single substrate flux), rather than in the inner workings of the biofilm (Bishop and Rittmann, 1995).

In this paper the comparison of 1-D biofilm reactor models that use simplified (fixed-order, i.e. zero- and first-order) and Monod kinetics is presented. Two different situations have been compared: one rate-limiting substrate with or without liquid film diffusion.

This kind of model has been validated using data obtained from two tertiary nitrification bench scale reactors that implement a new technology, the so-called "pure oxygen moving bed biofilm reactor (PO-MBBR)" technology (Bonomo *et al.*, 2000). In fact, tertiary nitrification is one of the biochemical process that does not require the use of multi-substrate, multi-species biofilm models due to the lack of competition between autotrophs and heterotrophs for oxygen.

Model description

General model: one rate-limiting substrate with negligible liquid film diffusion

The general 1-D biofilm model developed is based on the following four fundamental hypotheses:

1. a homogeneous biofilm grows on a solid, inert and impervious substratum, with a thickness L_f at steady state and a plane surface parallel to the substratum: homogeneity regards both physical and biological properties;
2. within the biofilm a single biochemical (redox) reaction takes place: only one soluble substrate, having a concentration S_f variable in the direction normal to the substratum (x axis with origin on biofilm surface), is the rate-limiting substrate; the reaction (removal) rate per unit biofilm volume $r_{v,f}$ can be expressed as a function of the substrate flux into the biofilm J_f by means of a mass balance across an infinitesimal section of the biofilm;
3. the soluble substrate is transported across the biofilm by molecular diffusion: D_f is the molecular diffusion coefficient of the substrate within the biofilm according to Fick's law;
4. the effect of the liquid film diffusion can be neglected, therefore substrate concentration at the biofilm surface (biofilm/water interface) is the same for the bulk liquid (i.e. $S_s=S_b$).

The second-order differential equation that can be used (with proper boundary conditions) for defining the concentration profile of the substrate within the biofilm is obtained in its dimensionless form using the dimensionless groups σ (dimensionless substrate

concentration) and ξ (dimensionless distance into biofilm):

$$\frac{d^2\sigma(\xi)}{d\xi^2} = \frac{L_f^2}{D_f S_b} r_{v,f}\left(\sigma(\xi)\right) \tag{1}$$

The solution of Eq. (1) allows us to calculate the reaction (removal) rate per unit biofilm area r_a and the reaction (removal) rate per unit reactor volume $r_{v,r}$, by means of the two following equations:

$$r_a = J_f(0) = -D_f\left[\frac{dS_f}{dx}\right]_{x=0} = -\frac{D_f S_b}{L_f}\left[\frac{d\sigma}{d\xi}\right]_{\xi=0} \tag{2}$$

$$r_{v,r} = a \cdot r_a \tag{3}$$

Effect of liquid film diffusion

If, in contrast to hypothesis 4 of the general model, the effect of the liquid film diffusion cannot be neglected, a substrate concentration gradient can be observed between the bulk liquid and the biofilm surface (i.e. $S_b > S_s$), which are separated by a liquid film layer having a thickness L_w. Again, this phenomenon can be expressed by Fick's law, where D_w is the molecular diffusion coefficient of the substrate in water. As a consequence, Eq. (2) can be substituted by the following equation:

$$r_a = J_w = -D_w\left[\frac{dS}{dx}\right]_{-L_w \le x \le 0} = \frac{D_w}{L_w}\left(S_b - S_S\right) = k_w\left(S_b - S_S\right) = -D_f\left[\frac{dS_f}{dx}\right]_{x=0} \tag{4}$$

The use of Monod kinetics

Differently from Harremoës (1978), who has used simplified (fixed-order) kinetics for $k_{v,f}$ and has been able to calculate analytical solutions of Eq. (1) with proper boundary conditions, in this paper Monod kinetics have been preferred because continuous variable-order kinetics reflect in a better way the effects of the reduction of substrate concentration across the biofilm due to biochemical consumption and diffusional resistance. Monod kinetics and the use of the dimensionless groups δ (substrate concentration ratio) and σ (dimensionless substrate concentration) are illustrated in the following equation:

$$r_{v,f} = k_{0,f}\frac{S_f}{K_S + S_f} = k_{0,f}\frac{\sigma}{\delta^{-1} + \sigma} \tag{5}$$

The second-order differential equation obtained using Monod kinetics for the two different situations studied (lack or presence of liquid film diffusion) together with the proper boundary conditions are illustrated below:

$$\frac{d^2\sigma(\xi)}{d\xi^2} = \frac{L_f^2 k_{0,f}}{D_f S_b}\frac{\sigma}{\delta^{-1} + \sigma} = \frac{2}{\beta^2}\frac{\sigma}{\delta^{-1} + \sigma} = \frac{\alpha^2}{\delta}\frac{\sigma}{\delta^{-1} + \sigma} \tag{6}$$

One-rate-limiting substrate with negligible liquid film diffusion:

$$\begin{cases}[\sigma]_{\xi=0} = 1 \\ [d\sigma / d\xi]_{\xi=1} = 0\end{cases} \tag{7}$$

Effect of liquid film diffusion:

$$\begin{cases}[\sigma]_{\xi=0} = 1 \\ [d\sigma / d\xi]_{\xi=0} = -(D_w / D_f)(1 - \sigma_s) / \xi_w \\ [d\sigma / d\xi]_{\xi=1} = 0\end{cases} \tag{8}$$

Unfortunately the use of Monod kinetics does not allow us to calculate analytical solutions that can therefore be obtained by means of numerical methods.

Numerical approach and model implementation

The aim of the numerical approach is to solve the boundary value problem (BVP) of ordinary differential equations (ODE) formulated as follows (Engeln-Müllges and Uhlig, 1996):

$$y''(x) = g(x, y, y') \tag{9}$$

with boundary conditions:

$$\begin{cases} \alpha_1 y(a) + \alpha_2 y'(a) = A \\ \beta_1 y(b) + \beta_2 y'(b) = B \\ |\alpha_1| + |\beta_1| > 0 \\ \alpha_i \neq 0 \quad \beta_j \neq 0 \text{ for at least one index} \end{cases} \tag{10}$$

The existence and uniqueness of solution of such BVP is governed by the following conditions:

1. right-hand side function of Eq. (9) $g(x, y, y')$ has continuous first partial derivatives in the interval [a, b];
2. the sum $y^2+y'^2$ is finite in [a, b];
3. in the interval [a, b], two constants L and M ($0 \leq L, M \leq \infty$) exist that satisfy the following conditions:

$$0 < \frac{\partial g}{\partial y} \leq L \text{ and } \left|\frac{\partial g}{\partial y'}\right| \leq M \tag{11}$$

4. the constants α_1, α_2, β_1 and β_2 must satisfy the following conditions:

$$\begin{cases} \alpha_1 \alpha_2 \leq 0 \\ \beta_1 \beta_2 \geq 0 \end{cases} \tag{12}$$

The solution is obtained by means of the so-called Shooting Method, reducing the problem to an initial value problem (IVP) and determining by iterations the correct initial values. Implementation of the method was based upon an available software library in C language (Engeln-Müllges and Uhlig, 1996) suitably modified in order to avoid instability; the software has been run on a workstation HP 9000 (Quinto, 1998).

It is important to point that that the key parameters used to drive the simulation, the dimensionless groups α (biofilm constant), δ (substrate concentration ratio) and ξ_w (dimensionless liquid film layer thickness), hold all the physical and biological information about the system: α is linked to biofilm structure (mainly thickness L_f and molecular diffusion coefficient of the substrate D_f), δ is linked with substrate availability (substrate concentration in the bulk liquid S_b), while ξ_w is linked with diffusional resistance due to the liquid film layer (if not negligible).

Typical outputs of the software are:

- reaction (removal) rate per unit biofilm area r_a;
- dimensionless reaction rate κ;
- kinetic order o_a;
- substrate concentration at biofilm/substratum interface $\sigma(l)$.

The order of the reaction o_a has been obtained by analysing numerical results. Of course, it has been defined as first derivative of curve of reaction rate to substrate concentration in a log–log graph, as follows:

$$o_a(S_b, r_a) = \frac{d(\ln r_a)}{d(\ln S_b)} = \frac{S_b}{r_a}\frac{dr_a}{dS_b} = \frac{\delta}{\kappa}\frac{d\kappa}{d\delta} = o_a(\delta, \kappa) \tag{13}$$

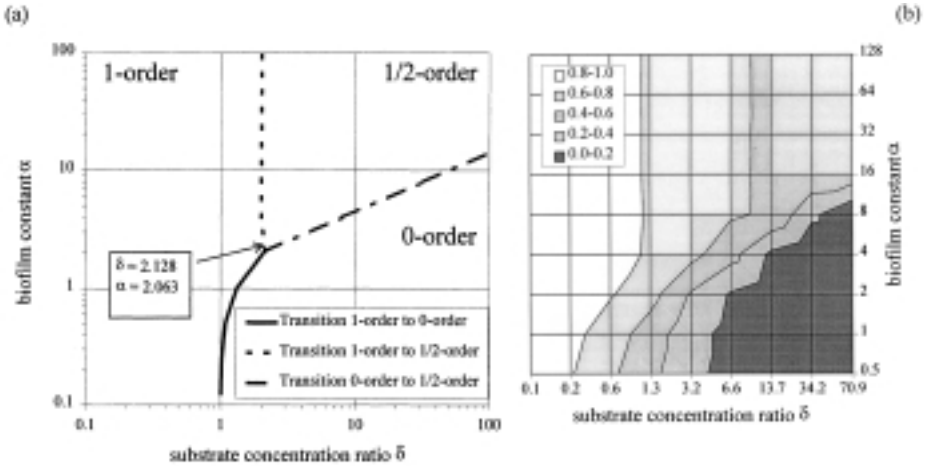

Figure 1 Order of the reaction o_a in the two-dimensional space biofilm constant α-substrate concentration ratio δ: (a) simplified and (b) Monod kinetics

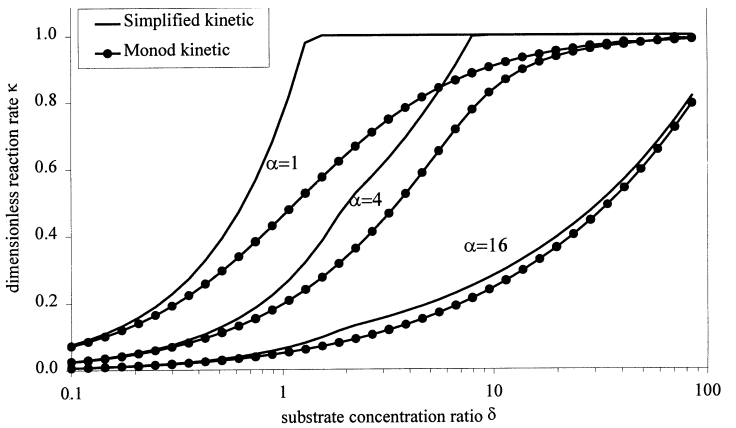

Figure 2 Dimensionless reaction rate κ versus substrate concentration ratio δ: differences between simplified and Monod kinetics for selected values of the biofilm constant α

Results and discussion

One rate-limiting substrate with negligible liquid film diffusion

Figure 1 shows the order of the reaction o_a in the two-dimensional space biofilm constant α-substrate concentration ratio δ, for simplified and Monod kinetics under two fundamental hypotheses:

- existence of only one rate-limiting substrate and
- negligible effect of liquid film layer on substrate diffusion into the biofilm.

The application of simplified (fixed-order, i.e. zero- and first-order) kinetics, as proposed by Harremoës (1978), results in only three different orders of the reaction at reactor level (Figure 1a):

- zero-order (zero-order kinetic inside a fully penetrated biofilm),
- half-order (zero-order kinetic inside a partly penetrated biofilm) and
- first-order (first-order kinetic inside the biofilm).

On the contrary, the application of Monod kinetic allows us to describe the continuous variation of kinetic order (Figure 1b). It is possible to observe that the transition lines plotted on Figure 1a have been substituted by a gradual transition between zero- and first-order. The order o_a increases (and simultaneously dimensionless removal rate κ decreases) when

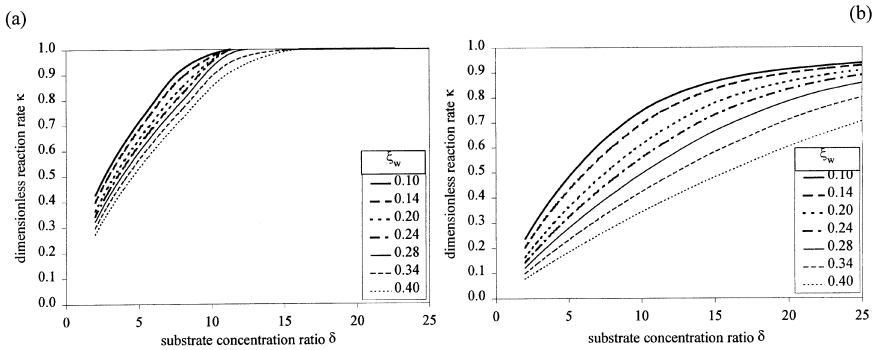

Figure 3 Dimensionless reaction rate κ versus substrate concentration ratio δ: differences between (a) simplified and (b) Monod kinetics for selected values of the dimensionless liquid film layer thickness ξ_w (α=4)

a increases (reduced substrate penetration) and δ decreases (reduced substrate available in the bulk liquid).

Figure 2 shows the relationship between dimensionless reaction rate κ and substrate concentration ratio δ for simplified and Monod kinetics for selected values of the biofilm constant α (1, 4 and 16). It is clear that for thin biofilms the simplified approach overestimates the removal rates, while for thick ones results are similar. This can be explained considering that thick biofilms can compensate the reduced reaction rate due to the application of Monod kinetic with a thicker active layer of biomass.

An important result is that observed kinetic orders higher than 0.5 do not require necessarily to be explained by means of liquid film diffusion effects.

Effect of liquid film diffusion

Figure 3 shows the relationship between dimensionless reaction rate κ and substrate concentration ratio δ for simplified and Monod kinetics for selected values of the dimensionless liquid film layer thickness ξ_w (that is, when the liquid film diffusion cannot be neglected). It can be observed that the simplified approach overestimates the removal rates, that is, underestimate the kinetic order. This can be explained considering the lower effect of concentration reduction due to liquid film diffusion on zero-order kinetics.

An important result is that, in order to justify the observed kinetic order higher than 0.5, the simplified approach evaluates liquid film layers thicker than the actual ones.

Conclusions

A theoretical study supported by some experimental tests has been carried out with the aim of comparing 1-D biofilm reactor models that use simplified (fixed-order, i.e. zero- and first-order) and Monod kinetics. The models assume biofilm as a homogeneous layer containing uniformly distributed bacterial cells.

Two different situations have been compared: one rate-limiting substrate with or without liquid film diffusion. The results obtained show that the use of a simplified kinetic approach compared to the Monod kinetic approach determines (1) an unjustified overestimate of the removal rate, especially for thin biofilm, and (2) an excessive overestimate of the liquid film layer thickness necessary to justify high kinetic orders.

A lot of literature produced in the 1990s shows that biofilm structure is not homogeneous but that a 3-D porous structure exists. A complex population dynamic can also be recognised: the result is that bacterial cells are not uniformly distributed but lie in clusters and that competition between species (e.g. autotrophs and heterotrophs) plays an important role. Nevertheless 1-D models still now continue to be the only ones that can reasonably support process engineers in biofilm reactor design, due to their intrinsic simplicity and the need of

small sets of input data and parameters that can be obtained theoretically or often empirically. Computer models that implement numerical methods can be used to solve the differential equations containing Monod kinetics instead of simplified (fixed-order) kinetics.

Nomenclature

Symbols used in the text, defined as carefully as possible according to Grau *et al.* (1982), are summarised below.

Symbols

a	biofilm surface area per unit reactor volume [L^2L^{-3}]
D	molecular diffusion coefficient [L^2T^{-1}]
$k_{0,f}$	zero-order reaction rate constant [$M\ L^{-3}T^{-1}$]
$k_{l,f}$	first-order reaction rate constant [T^{-1}]
K_S	saturation constant [ML^{-3}]
k_w	mass transfer coefficient in the liquid film [LT^{-1}]
J	substrate flux [$ML^{-2}T^{-1}$]
L	thickness [L]
r_a	reaction rate per unit biofilm area [$ML^{-2}T^{-1}$]
r_v	reaction rate per unit volume [$ML^{-3}T^{-1}$]
S	substrate concentration [ML^{-3}]
x	distance into biofilm (from biofilm surface) [L]

Dimensionless parameters

$\alpha = \sqrt{k_{1,f}L_f^2 / D_f} = \sqrt{k_{0,f}L_f^2 / (D_f K_S)} = \sqrt{2\delta / \beta^2}$ biofilm constant

$\beta = \sqrt{2D_f S_b / (k_{0,f}L_f^2)} = \sqrt{2\delta / a^2}$ penetration ratio

$\delta = S_b / K_S = \alpha^2\beta^2 / 2$ substrate concentration ratio

$\kappa = r_a / r_{a,0} = r_a / (k_{0,f}L_f)$ dimensionless reaction rate

$\lambda = (k_w S_b) / (k_{1/2,a}S_b^{1/2})$ liquid film diffusion/biofilm diffusion ratio

$o_a = \frac{S_b}{r_a}\frac{dr_a}{dS_b} = \frac{\delta}{\kappa}\frac{d\kappa}{d\delta}$ order of the reaction

$\sigma = S_f / S_b$ dimensionless substrate concentration

$\xi = x / L_f$ dimensionless distance into biofilm (from biofilm surface

Subscripts

b	bulk liquid
f	biofilm
p	maximum substrate penetration
r	reactor
s	biofilm surface (i.e. biofilm/water interface)
w	water, liquid film

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