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Modeling biofilm and floc diffusion processes based on analytical solution of reaction-diffusion equations

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Abstract

Biofilm modeling is often considered as a complex mathematical subject. This paper evaluates simple equations to describe the basic processes in a biofilm system with the main aim to show several interesting applications. To avoid mathematical complexity the simulations are carried out in a simple spreadsheet. Frequently, only the solution for zero-order reaction kinetics of the reaction-diffusion equation is used (better known as half-order kinetics). A weighted average of the analytical solutions for zero- and first-order reactions is proposed as basic and useful model to describe steady-state (in biofilm composition) biofilm reactors. This approach is compared with several modeling approaches, such as the simple solution for zero-order reaction and more complex ones (i) direct numerical solution for the diffusion equations, (ii) 1-D AQUASIM and (iii) 2-D modeling. The systems evaluated are single and multiple species biofilms. It is shown that for describing conversions in biofilm reactors, the zero-order solution is generally sufficient; however, for design purposes large deviations of the correct solution can occur. Additionally, the role of diffusion in flocculated and granular sludge systems is discussed. The relation between the measured (apparent) substrate affinity constant and diffusion processes is outlined.

Keywords: Biofilm modeling; Flocs; Apparent affinity constant; Reaction-diffusion kinetics

1. Introduction

Biofilms are complex microbial ecosystems in which several physical, chemical and biological processes take place simultaneously. In order to evaluate such systems, mathematical models could be very helpful. However, mathematical complexity is often a drawback for the application and even understanding of detailed models like those proposed by Wanner and Gujer (1986) or Picioreanu et al. (1998). Simplification of these mathematical models has been the subject of several papers (Harris and Hansford, 1978; Harremoës, 1978; Sáez and Rittmann, 1992; Rauch et al., 1999). Assuming zero-order kinetics for the conversion in the biofilm leads to a simple mathematical expression for the flux of substrate over the biofilm interface. Because of its form, this expression is known as half-order kinetics (Harremoës, 1978). The assumption of zero-order kinetics in biofilms to compute fluxes of substrate into the biofilm and the concentration of substrate in the bulk liquid can produce important deviations from the rigorous solution. This paper will evaluate these potential deviations and proposes a more adequate analytical treatment of biofilm processes.

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Notation

a	specific surface area in flocs (m^{-1})
A	area (m^2)
b	overall decay rate (s^{-1})
C	concentration ($kg\,m^{-3}$)
d	diameter (m)
D	diffusion coefficient ($m^2\,s^{-1}$)
J	flux ($kg\,m^{-2}\,s^{-1)}$
K	half saturation constant ($kg\,m^{-3}$)
L	biofilm thickness (m)
q	substrate-specific conversion rate ($kg\,kg^{-1}\,s^{-1}$)
Q	volumetric flow rate ($m^3\,s^{-1}$)
r	volumetric conversion rate ($kg\,m^{-3}\,s^{-1}$)
t	time (s)
V	volume (m^3)
x	distance inside biofilm (at interface $x = 0$) (m)
Y	yield coefficient ($kg\,kg^{-1}$)
δ	penetration depth of a substrate (m)

Superscripts

biofilm	biofilm phase
in	with respect to inflow
max	maximum
mod	modified
l/b	liquid–biofilm interface
1	first-order reaction rate
0	zero-order reaction rate

Subscripts

A	autotrophic biomass
H	heterotrophic biomass
i	a certain compound
p	particle (relative to the floc)
sph	spherical (relative to the floc)
X	biomass

Diffusion plays not only a role in biofilm processes but also in activated and granular sludge systems. Certainly, for activated sludge processes this is often neglected. This effect of diffusion processes is effectively reflected in affinity constants for activated sludge processes, which are usually one order of magnitude higher than those reported for single suspended cells. The relation between floc diffusion and affinity constant will be evaluated with the proposed solutions for reaction-diffusion equations.

The substrate affinity constant is a biological parameter characteristic of the particular microbial species. In systems where microorganisms grow as aggregates or biofilm, an apparent affinity constant is measured. Due to diffusion-reaction processes inside the aggregate, the concentration observed by the microorganisms in the aggregate is lower than in the bulk liquid. This leads to a higher observed affinity constant if the reactivity of the aggregate is modeled by Monod kinetics (see below, Eq. (3)).

Values of K_S found in literature for activated sludge systems are determined in diffusion-limiting conditions, due to the presence of flocs. For instance, Parker et al. (1975) determine the half-saturation coefficient for dissolved oxygen for nitrifying bacteria in a range of 0.5–2.0 g O_2/m^3, taking for illustrative purposes a value of 1.3 g O_2/m^3. In Activated Sludge Model No. 1 this parameter is assumed as 0.4 g O_2/m^3 (Henze et al., 1987). Stenstrom and Song (1991) determine a range for this kinetic parameter of 0.45–0.56 g O_2/m^3, for activated sludge systems. For pure cultures much lower values are usually reported (0.05–0.3 g O_2/m^3 Hunik et al., 1994; Williamson and McCarthy, 1976). The wide range of experimental values for this coefficient and the large difference between pure (suspended) culture and activated sludge systems can be explained by the diffusion effect, as it was discussed by Beccari et al. (1992).

In this paper an averaged approach of analytical solutions for first and zero-order reaction kinetics is presented and compared with other biofilm modeling approaches. It is assumed that more complex models can produce more accurate solutions. This analysis will be carried out as a function of the dimensionless ratio C_S/K_S, showing how the large differences in experimental K_S values reported in literature affect the accuracy of the analytical treatment proposed.

2. Model description

A biofilm reactor can be generically described as a system with three separate phases, the biofilm, gas and liquid phase. The substrates are added to the reactor by a gas or liquid flow.

In order to use only a rather simplified description of a generic biofilm reactor, a set of assumptions have been considered in this paper: (i) For a first treatment, the liquid phase will be described as a completely mixed compartment. (ii) The biofilm is described as a one-dimensional (1-D) system with lateral concentration gradients and heterogeneity in the biofilm is considered as of marginal influence. (iii) The gas phase as such is not separately described. If needed (e.g. when there is a significant change in gas phase concentrations), a gas phase could however be easily added to the description.

(iv) Free biomass is not considered as active in the mathematical description of the biofilm reactor. This can be easily included in the description, and should be done if real systems have to be described. It would lead however to more difficult to read equations. (v) External mass transfer has been neglected in this paper. The mass transfer coefficient for flat rigid interfaces can be obtained from standard process engineering relations (Perry et al., 1997). For biofilms, this coefficient has to be adjusted slightly (around 15% lower according to Nicolella et al. (2000)) to account for the fact that the biofilm is not fully rigid.

2.1. Mass balances

2.1.1. Substrate in the bulk liquid

The general description of conversion in a completely mixed liquid phase of a biofilm reactor in steady state is based on a balance for the compounds of interest, which can be written as

$$Q(C_i^{\text{in}} - C_i^{\text{l}}) = J_i^{\text{biofilm}} A^{\text{biofilm}}, \tag{1}$$

where Q is the volumetric flow rate, C_i^{in} and C_i^{l} are the concentrations of compound i in the inflow and bulk liquid, respectively, A is the surface of the biofilm in contact with the liquid phase, and J_i^{biofilm} is the flux of compound i over the biofilm interface.

Eq. (1) states that the difference between the mass of substrate in the influent and effluent is transferred towards the biofilm where it subsequently has been converted. The flow pattern of the liquid phase in some of the different biofilm reactors found in literature cannot be correctly described with a single well-mixed compartment. Successful description of the different flow patterns can be achieved using multi-compartment models (Levenspiel, 1972). The application of these flow models will allow the application of the general methodology described in this paper for a wide number of different biofilm systems.

2.1.2. Substrate in the biofilm

In the biofilm, the substrate is transported by diffusion due to the substrate gradient in x-direction (distance inside biofilm) and is converted by the biomass present in the biofilm. For a homogeneous flat biofilm in steady state this can be expressed as

$$D_i \frac{\mathrm{d}^2 C_i}{\mathrm{d}x^2} + r_i = 0, \tag{2}$$

where D_i is the diffusion coefficient of substrate i and r_i is the substrate volumetric conversion rate of substrate i.

Differential Equation (2) can only be solved analytically for first- or zero-order reaction kinetics. For the typical substrate affinity kinetics for biological processes (Monod equation), Eq. (2) can only be solved numerically. The substrate volumetric conversion rate (r_i) has then the following expression:

$$r_i = q_i^{\max} \frac{C_i}{C_i + K_i} C_{\text{X}}, \tag{3}$$

where C_{X} is the biomass concentration in the biofilm, $q_i^{\max}$ is the maximum specific substrate conversion rate (ratio-specific growth rate/yield biomass-substrate) and K_i is the affinity constant of substrate i.

At high substrate concentration ($C_i \gg K_i$), the reaction can be considered zero order, while at very low concentration ($K_i \gg C_i$) the conversion can be considered first order. The analytical solutions for zero- and first-order reaction kinetics are given by the following expressions (Levenspiel, 1972; Harris and Hansford, 1978; Harremoës, 1978):

2.1.2.1. Zero-order kinetics. The analytical solution for zero-order kinetics is obtained separately for fully or partially penetrated biofilms. The flux of substrate into a partially penetrated flat biofilm for zero-order kinetics ($J_i^{\text{biofilm,0}}$) is

$$J_i^{\text{biofilm,0}} = \sqrt{2 D_i q_i^{\max} C_{\text{X}}} \sqrt{C_i^{\text{l/b}}}, \tag{4}$$

where $C_i^{\text{l/b}}$ is the concentration of substrate i at the interface liquid–biofilm, as external mass transfer is neglected in the applications discussed in this paper, $C_{\text{i}}^{\text{l/b}}$ is here equal to the concentration in the bulk liquid (C_i^{l}). The first square root in Eq. (4) is a constant for a certain biofilm. This is effectively the constant used in the half-order kinetics approach (Harremoës, 1978).

A penetration depth (δ) can be defined below which the substrate concentration equals zero:

$$\delta = \sqrt{\frac{2 D_i C_i^{\text{l/b}}}{q_i^{\max} C_{\text{X}}}}. \tag{5}$$

To investigate the diffusion processes in activated sludge flocs, spherical coordinates are used, leading to following differential equation:

$$D_i \left(\frac{\mathrm{d}^2 C_i}{\mathrm{d}r^2} + \frac{2}{r} \frac{\mathrm{d}C_i}{\mathrm{d}r} \right) - r_i = 0, \tag{6}$$

where r is the radial distance from the centre in the floc particle. The analytical solution of Eq. (6) for zero-order kinetics is

$$J_i^{\text{sph,0}} = \frac{q_i^{\max} C_{\text{X}} (r_{\text{p}}^3 - (r_{\text{p}} - \delta_{\text{sph}})^3)}{3 r_{\text{p}}^2}, \tag{7}$$

where r_{p} is the floc radius. The penetration depth (δ_{sph}) can be determined from

$$3\delta_{\text{sph}}^2 - \frac{2\delta_{\text{sph}}^3}{r_{\text{p}}} = \frac{6 D_i C_i^{\text{l/b}}}{q_i^{\max} C_{\text{X}}}. \tag{8}$$

Eq. (8) can be solved either using a manual iterative process or in case of using an EXCEL spreadsheet, the SOLVER tool could be used (see also Section 2.2.4).

When the biofilm thickness is less than the penetration depth, the full biofilm is active and the flux can be evaluated directly from: For flat biofilms

$$J_i^{\text{biofilm}} = L_f q_i^{\max} C_X. \tag{9}$$

For spherical coordinates:

$$J_i^{\text{sph,zero}} = \frac{q_i^{\max} C_X r_p}{3} \tag{10}$$

2.1.2.2. First-order kinetics. The flux of substrate into a flat biofilm for first-order kinetics ($J_i^{\text{biofilm,1}}$) is (Levenspiel, 1972; Harris and Hansford, 1978; Harremoës, 1978)

$$J_i^{\text{biofilm,1}} = \frac{q_i^{\max} C_X L_f C_i^{1/b}}{K_i}\,\varepsilon$$

with

$$\varepsilon = \frac{\tanh\,\beta}{\beta}; \quad \beta = \sqrt{\frac{q_i^{\max} C_X L_f}{D_i K_i}}, \tag{11}$$

where $J_i^{\text{biofilm,1}}$ is the flux of substrate through the biofilm for first-order kinetics and L_f is the biofilm thickness.

For a first-order reaction rate there is mathematically no point inside the biofilm where the substrate concentration becomes equal to zero; therefore, a penetration depth for the limiting substrate cannot be rigorously defined.

The substrate diffusion coefficient in biofilm in Eqs. (4), (5) and (11) is lower than the coefficient in water due to the presence of polymers, inorganic particles and microbial cells which obstruct the diffusion of solutes. Since in most biofilms the (bound) water volume fraction is larger than 0.9, very often the diffusion coefficient in water is used (Westrin and Axelsson, 1991; Beuling et al., 2000).

2.1.2.3. Overall kinetics. The flux of substrate through the biofilm (J_i^{biofilm}) may be estimated as the weighted average of the zero- and first-order reaction rate:

$$J_i^{\text{biofilm}} = \left(\frac{C_i^{1/b}}{C_i^{1/b} + K_i}\right) J_i^{\text{biofilm,0}} + \left(1 - \frac{C_i^{1/b}}{C_i^{1/b} + K_i}\right) J_i^{\text{biofilm,1}}. \tag{12}$$

This approach had been used before in other biochemical fields, i.e. immobilized biocatalysts (Kobayasi et al., 1976; Yamane, 1981). The advantage of an expression based on analytical solutions, in addition to simplicity, is that the effect of each term, variable or parameter on the overall flux Eq. (12) can be directly analyzed. That is not possible when more complex solutions are used (for instance, numerical solution, or more complex 2-D/3-D biofilm models, in which the flux equation is not an explicit mathematical expression). The advantage of the application of a weighted average of analytical solutions is that these simple equations are providing a good tool to understand biofilm processes. At the same time, a simple mathematical procedure to calculate solutions is required and small deviations from more complex numerical treatments are obtained as it will be discussed in the present paper.

2.1.3. Biomass

The general biomass balance in steady state for a biofilm process can be written as

$$J_i^{\text{biofilm}} Y_i - b^i C_{X_i} L_f = 0, \tag{13}$$

where the first term is the production of biomass (Y_i is the yield biomass/substrate) and the second one represents the decrease in biomass due to inactivation, detachment and endogenous respiration. The overall decay rate coefficient b_i can be computed with the following expression:

$$b^i = b^i_{\text{inac}} + b_{\text{det}} + b^i_{\text{resp}}. \tag{14}$$

2.2. Process model

The conversions in a biofilm reactor can now be solved by coupling the mass balance equation for substrate (1) and biomass (13), taking into account the relevant flux Equations (4), (11) and (12). For a set of operating conditions and a given system, influent volumetric flow rate (Q), biofilm surface area (A) and influent concentration (C_i^{in}) will be known. For known microorganisms the kinetic constants, yield and maximum biomass concentration in the biofilm can be estimated or fixed. The only unknown variables of the two equations system are the outflow concentration of substrate (which represents the conversion in the reactor) and biofilm thickness (L_f). The system has to be solved iteratively satisfying the condition that in steady state the flux towards the biofilm (defined by Eq. (12)) satisfies Eq. (1) and (13).

2.2.1. One biological conversion process

For biological reactions several compounds are converted simultaneously (e.g. COD, Oxygen, and N-source). The conversion of all these compounds is linked by the stoichiometric equation describing the biological growth process. One of these compounds will be the rate-limiting compound for which the conversion rate (Eq. (3)) has to be calculated as described above, all other components will be converted relative to their

stoichiometric factor. The compound with the relatively lowest transport rate will be the rate-limiting compound. The rate-limiting compound will have the lowest outcome for the following relation (Andrews, 1988):

$$\frac{D_i C_i^{\mathrm{l}}}{Y_i}. \tag{15}$$

After the rate-limiting compound has been defined, it has to be evaluated whether this compound is fully or partially penetrating. This can be done by calculating the penetration depth for zero-order rate by Eq. (5).

2.2.2. Two or more biological conversion processes & biofilm architecture

If two or more biological reactions occur, an assumption has to be made on the architecture of the biofilm. From experimental and modeling results some general assumptions can be made on the biomass distribution with biofilm depth (Wanner and Gujer, 1986; van Loosdrecht et al., 1995; Okabe et al., 1999). The main ordering of biomass is based on the type electron acceptor or redox potential. At the outside will be the conversion with the highest redox potential (general aerobic oxidation), while in the inside the conditions get more reduced (anoxic, sulfate reducing and methanogenic). Within a redox zone a further biomass distribution can occur, where faster growing bacteria are generally found at the outside (e.g. aerobic heterotrophs or acidifyers) while slower growing bacteria (nitrifyers or methanogens) are more inside the biofilm. This is especially true when there are large differences in growth rate. When the differences are small (e.g. ammonium oxidation and nitrite oxidation) one has to consider that the bacteria are mixed. In that case, the relative composition of the biomass can be obtained from the ratio of the product of yield coefficient and the converted amount.

As a simplification we assumed here that the three forms of biomass (heterotrophs, autotrophs and inerts) are homogeneously distributed in the biofilm. That is the simplest way to treat a multi-species biofilm. Nevertheless, to take into account the main effect of the real (layered) biofilm structure, limiting conditions for a common substrate for the two species (i.e. oxygen) will always be applied first for the species with lowest growth rate (i.e. autotrophs).

The competition for space in the biofilm has been taken into account considering the following balance for the total biomass density in the biofilm:

$$C_{\mathrm{Xf}} - C_{\mathrm{XH}} - C_{\mathrm{XA}} - C_{\mathrm{XI}} = 0, \tag{16}$$

where the total biomass concentration in the biofilm (C_{Xf}) has been taken as $10^4\,\mathrm{g\,m^{-3}}$ (Characklis and Marshall, 1989; Morgenroth et al., 2004) in all the cases. C_{XH}, C_{XA} and C_{XI} are concentrations of heterotrophic, autotrophic and inert biomass, respectively.

2.2.3. Kinetics for multiple limiting substrates

Multiplication of Monod terms has been treated as a mathematical way to express the presence of multiple limiting substrates. The main difficulty will be to handle the multiplication of Monod terms for the two substrates. The mathematical expression used to describe the presence of multiple substrates has also been suggested as the minimum of both terms by several authors (for instance in Hunik et al., 1994). In the present study, the approach used is similar to ASM 1 (Henze et al., 1987), modifying the maximum specific substrate conversion rate ($q_i^{\max}$) with the Monod term (evaluated in the interface liquid–biofilm) corresponding to the non-limiting substrate:

$$r_i = q_i^{\max} \frac{C_i^{\mathrm{l/b}}}{C_i^{\mathrm{l/b}} + K_i} \frac{C_{\mathrm{O_2}}^{\mathrm{l/b}}}{C_{\mathrm{O_2}}^{\mathrm{l/b}} + K_{\mathrm{O_2}}} C_{\mathrm{X}} = q_i^{\max,\mathrm{mod}} \frac{C_{\mathrm{limiting}}^{\mathrm{l/b}}}{C_{\mathrm{limiting}}^{\mathrm{l/b}} + K_{\mathrm{limiting}}} C_{\mathrm{X}}, \tag{17}$$

where $q_i^{\max,\mathrm{mod}}$ is the maximum specific substrate conversion rate modified with the non-limiting saturation terms. Leading to an expression equivalent to Eq. (3), allowing the same procedure can be applied.

2.2.4. Solving the problem with a simple spreadsheet

To solve the problem by using the weighted average approach, a simple spreadsheet is used to obtain the result. The mass balances can be directly introduced and it is possible to find the steady-state solution using either manual iteration or with the aid of an optimization tool (SOLVER tool in EXCEL), which allows to carry out a constrained multivariable optimization. A set of guidelines is given below to describe briefly how the calculations were carried out. For details, the EXCEL file can be downloaded from http://www.elsevier.com.

In the case of the automatic iterative process with the optimization tool, for instance, once a set of parameters and conditions is fixed, the target cell will contain one of the mass balances (e.g. biomass balance, Eq. (13)). The variables for the optimization method (adjustable cells) will be the concentration of rate-limiting substrate in the interface liquid-biofilm ($C_i^{\mathrm{l/b}}$) and the biofilm thickness (L_{f}) whereas the substrate balance in the reactor (Eq. (1)) is introduced as a constraint.

For a multi-species biofilm system, the mass balance equation (16) is used as target cell in the optimization problem, and the constraints are the substrate balance in the reactor (for heterotrophs and autotrophs, Eq. (1)) and the biomass balance (for heterotrophs and autotrophs, Eq. (13)). The variables (adjustable cells) are substrate concentration of COD and N in the

liquid–biofilm interface, detachment rate (b_{det}) for heterotrophs (assuming the same value for autotrophs and inerts) and biomass density for heterotrophs and autotrophs.

Moreover, for the case of multiple limiting substrates a new constraint is introduced and the modified maximum specific substrate conversion rate ($q_i^{max,mod}$) must be declared as new variable in the optimization problem (new adjustable cell), because the outflow substrate concentration of the non-limiting compound $\left(C^{l/b}_{non\text{-}limiting}\right)$ is not known a priori. The constraint is

$$q_i^{max,mod} - q_i^{max} \frac{C^{l/b}_{non\text{-}limiting}}{C^{l/b}_{non\text{-}limiting} + K_{non\text{-}limiting}} = 0. \quad (18)$$

To compute $q_i^{max,mod}$ the concentration $C^{l/b}_{non\text{-}limiting}$ needs to be estimated, leading to an iterative process that could be solved manually. With EXCEL this would be solved using an initial guessed value that will be further recalculated to accomplish Eq. (18) for the different values of concentration of the non-limiting substrate found in the automatic iterative process (SOLVER tool in EXCEL).

2.3. Stoichiometric model and reactor operating conditions

The stoichiometric matrix and kinetic expressions used are summarized in Table 1. The biological parameters and physical constants as well as the set of reactor conditions considered are presented in Table 2. The values are in the range of standard values used for heterotrophic and autotrophic biomass in the Activated Sludge Model No. 1 (ASM 1, Henze et al., 1987).

3. Model performance

3.1. Numerical versus analytical solutions

To analyze the results obtained with the weighted average approach described in Eq. (12), a set of different biofilm operating conditions were simulated for a heterotrophic flat biofilm in which the liquid phase is considered to be completely mixed. The values obtained by the weighted average approach were compared with results obtained by numerically solving the mass balance (Eq. (2) using the substrate volumetric conversion described in Eq. (3)). For numerical integration a high accuracy orthogonal collocation method (Finlayson, 1972) was used on a grid of 14 nodes in the biofilm.

For a given set of parameters (described in Tables 1 and 2), the mass balances described by Eqs. (1) and (13) have been solved to determine the steady state in a wide range of inflow substrate concentrations. Two typical situations have been chosen: the description of an existing biofilm reactor, or the design of a new biofilm reactor.

3.1.1. Describing existing reactor systems

When an existing reactor is described the reactor volume and influent are the input parameters for the calculation (i.e. in Figs. 1–3 the reactor loading is a known variable) and the effluent composition resulting from the predicted biofilm conversion is calculated. To study the deviation between the weighted average and zero-order approaches with respect to the numerical solution, the calculated flux of rate-limiting substrate and outflow substrate concentration has been plotted against the reactor loading of the rate-limiting substrate concentration (Fig. 1 for the weighted average approach and Fig. 2 for the zero-order approach).

Table 1
Stoichiometric matrix and kinetics

Processes	Microorganisms			Substrates			Rate laws
	C_{XH}	C_{XA}	C_{XI}	C_S	C_N	C_{O_2}	
Heterotrophs							
1. Growth	1			$-1/Y_H$		$-(1-Y_H)/Y_H$	$\mu_{max,H}\frac{C_S}{C_S+K_S}\frac{C_{O_2}}{C_{O_2}+K_{O_2,H,g}}C_{XH}$
2. Inactivation	−1		1				$b_{ina,H}C_{XH}$
3. Endogenous respiration	−1					−1	$b_{resp,H}\,C_{XH}\frac{C_{O_2}}{C_{O_2}+K_{O_2,H,resp}}$
Autotrophs							
4. Growth		1			$-1/Y_A$	$-\frac{4.57-Y_A}{Y_A}$	$\mu_{max,A}\frac{C_N}{C_N+K_N}\frac{C_{O_2}}{C_{O_2}+K_{O_2,A,g}}C_{XA}$
5. Inactivation		−1	1				$b_{ina,A}C_{XA}$
6. Endogenous respiration		−1				−1	$b_{resp,A}\,C_{XA}\frac{C_{O_2}}{C_{O_2}+K_{O_2,A,resp}}$

In section Numerical versus analytical solutions, the rate laws for heterotrophs have been simplified to: $\mu_{max}(C_S/(C_S+K_S))\,C_{XH}$ for growth (1) and $b_{resp,H}C_{XH}$ for endogenous respiration (3).

Table 2
Biological parameters, physical constants and reactor conditions

	Notation	Value	Units
Heterotrophs			
Maximum specific substrate conversion rate	$q_{S,H}^{max}$	9.52	$gCOD_S\,g^{-1}COD_X\,day^{-1}$
Monod saturation constant for COD	K_S	4.00	$gCOD_S\,m^{-3}$
Monod saturation constant for O_2, growth	$K_{O_2,H,g}$	0.2	$g\,m^{-3}$
Monod saturation constant for O_2, respiration	$K_{O_2,H,resp}$	0.2	$g\,m^{-3}$
Yield biomass/substrate	Y_H	0.63	$gCOD_X\,g^{-1}COD_S$
Maximum biomass density in the biofilm	C_{XH}	10000	$gCOD_X\,m^{-3}$
Inactivation rate coefficient	$b_{ina,H}$	0.08	day^{-1}
Respiration rate coefficient	$b_{resp,H}$	0.32	day^{-1}
Diffusion coefficient for substrate	D_S	0.0001	$m^2\,day^{-1}$
Autotrophs			
Maximum specific substrate conversion rate	$q_{S,A}^{max}$	4.17	$gCOD_S\,g^{-1}COD_X\,day^{-1}$
Monod saturation constant for ammonium	K_N	1.00	$gN\,m^{-3}$
Monod saturation constant for O_2, growth	$K_{O_2,A,g}$	0.5	$g\,m^{-3}$
Monod saturation constant for O_2, respiration	$K_{O_2,A,resp}$	0.5	$g\,m^{-3}$
Yield biomass/substrate	Y_A	0.24	$gCOD_{\underline{X}}\,g^{-1}\,N$
Maximum biomass density in the biofilm	C_{XA}	10000	$gCOD_X\,m^{-3}$
Inactivation rate coefficient	$b_{ina,A}$	0.03	day^{-1}
Respiration rate coefficient	$b_{resp,A}$	0.12	day^{-1}
Diffusion coefficient for substrate	D_N	0.00017	$m^2\,day^{-1}$
Diffusion coefficient for oxygen	D_{O_2}	0.0002	$m^2\,day^{-1}$
Reactor conditions			
Numerical versus analytical solutions section			
Volumetric flow-rate/biofilm area	Q/A	0.2	$m^3\,m^{-2}\,day^{-1}$
Detachment rate	b_{det}	0.4	day^{-1}
Common conditions			
Area of biofilm/liquid interface	A	0.1	m^2
Volumetric flow-rate	Q	0.02	$m^3\,day^{-1}$
Biofilm thickness	L_f	500	μm
Influent COD concentration	C_S^{in}	30	$gCOD_S\,m^{-3}$
Influent ammonium concentration	C_N^{in}	6	$gN\,m^{-3}$

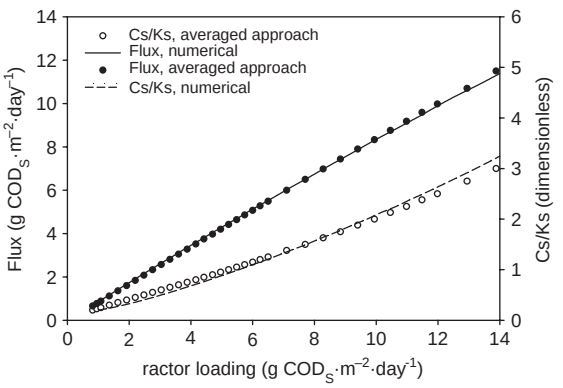

Fig. 1. Comparison between numerical and weighted average approach for a steady-state biofilm in a wide range of inflow concentrations in a well-mixed tank operating in continuous mode.

Using the weighted average approach the numerical results for flux and bulk concentration of substrate can be reproduced satisfactorily (Fig. 1) for the whole range of concentration, including the substrate concentration in the range of the substrate affinity constant (K_l). The relative deviation in calculated substrate flux is even smaller than the relative deviation in the calculated bulk concentration of substrate, at a fixed inflow load to the biofilm reactor. That is to say, the influent conditions (inflow concentration of substrate) are known, and the model is applied to compute both the flux and the bulk liquid concentration of substrate.

The zero-order approach can predict flux with relatively small deviations (e.g. for reactor loading about $2\,g\ COD_S\,m^{-2}\,day^{-1}$ deviation is 17% while for $14\,g\ COD_S\,m^{-2}\,day^{-1}$ it is 9%) when the reactor loading is fixed (and flux and bulk concentration are calculated), but the relative errors in the predicted bulk

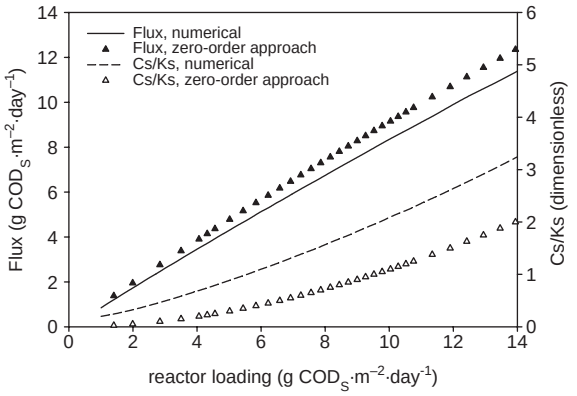

Fig. 2. Comparison between numerical and zero-order approach for a steady-state biofilm in a wide range of inflow concentrations in a well-mixed tank operating in continuous mode.

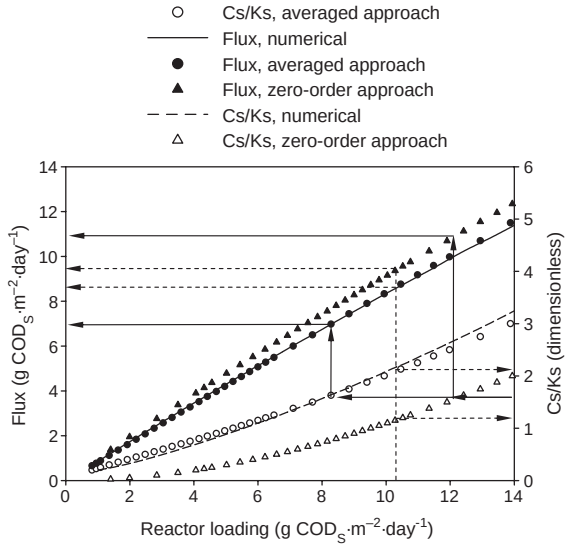

Fig. 3. Comparison between numerical and weighted average and zero-order approach for a steady-state biofilm in a wide range of inflow concentrations in a well-mixed tank operating in continuous mode. Arrows show differences when using the half-order approach for a fixed C_S/K_S (designing a biofilm reactor, solid arrows), and for a fixed reactor loading (describing existing reactor systems, dashed arrows).

concentration of substrate are larger, particularly for low C_S/K_S ratios (see dashed arrows in Fig. 3 as an example). This is logical since a first-order approximation assumes high C_S/K_S. It should be noted that the half-order approach should indeed not be used when substrate concentrations in the bulk liquid are around or below the substrate affinity constant.

3.1.2. Designing a biofilm reactor

In biofilm reactor design the influent characteristics and effluent requirements are input to the calculation of the desired reactor volume, which is calculated from the estimated required surface area and the flux of substrate towards the biofilm.

A comparison of model calculations can be made when the substrate flux is estimated with the model by fixing the effluent concentration of substrate (i.e. the bulk liquid concentration of substrate). This comparison is shown in Fig. 3 (solid arrows) and Fig. 4. In Fig. 3, it is possible to obtain the estimation of flux by fixing either the reactor loading or the bulk concentration of substrate. Therefore, the representation selected in Figs. 1–3 is more general than the type of graph presented in Fig. 4. In addition, in Fig. 3 dashed arrows are included for the case of "describing an existing reactor" (where reactor loading is fixed, already discussed in Section 3.1.1). As it can be seen in Fig. 3, the deviations in the estimated flux for both describing and designing applications are strongly different.

To further analyze why these different deviations are produced in both cases (describing and designing reactors), the error in the resolution of the differential equation (2) is compared directly for the case when the effluent concentration of rate-limiting substrate is fixed (see Fig. 4). To plot Fig. 4 the mass balance stated in Fig. 1 is not used, which is the main difference between describing and designing in terms of calculations. When applying mass balance in Eq. (1), for the case of describing an existing biofilm reactor, final deviations in flux are smaller. In addition, when in the design, the reactor loading (i.e. inflow concentration of substrate) is estimated, also a large deviation for the case of the zero-order solution occurs. Usually, the inflow concentration is fixed and known, and for this reason to represent the

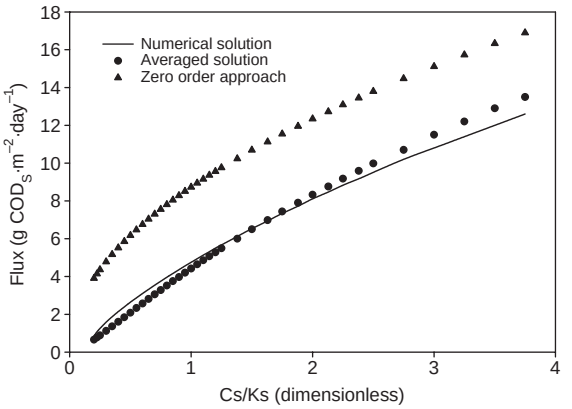

Fig. 4. Direct comparison of numerical, weighted average and zero-order approach in the resolution of Eq. (2). Deviations of both approaches are different from the case of a reactor operating in continuous mode.

flux versus the reactor loading is considered as more common and useful.

To estimate the flux by using the bulk concentration of substrate, the zero-order approach will have important deviation from numerical or weighted average approaches. This means that if the objective or application of the calculations is to obtain the flux using the bulk concentration of substrate in the reactor, the result computed with the zero-order approach will have important deviations as it is presented in Figs. 3 and 4. In Fig. 3 it is possible to compare both calculations: the one with a known reactor loading (the inflow concentration of substrate known) and the one computed keeping the bulk concentration of substrate constant.

The relative error for the rate-limiting substrate concentration in the outflow has also been plotted (Fig. 5) as percentage conversion in order to take into account the relative value of the outflow concentration with respect to the reactor loading. This provides a better idea of the deviation, because the relative error in terms of outflow concentration can be high whereas the absolute difference is not. The expression used is

$$\text{conversion } (\%) = \frac{C_S}{C_{in}} 100. \quad (19)$$

The deviation in terms of flux for the weighted average approach is not significant. In the case of the substrate concentration in the outflow, the differences are higher, but less than 30% in all cases, and less than 5% for inflow concentrations lower than $30\,g/m^3$ ($C_S/K_S > 1.1$).

In the case of the zero-order approach, deviations are more important. For $C_S/K_S > 15$ deviation from numerical solution in terms of flux is less than 10% (data not shown in Fig. 4), whereas the differences are lower than 10% in terms of conversion for the entire range of C_S/K_S (as can be observed in Fig. 5). It is clear that when the reactor concentration (or effluent concentration) is taken as known the square root kinetics give generally large errors.

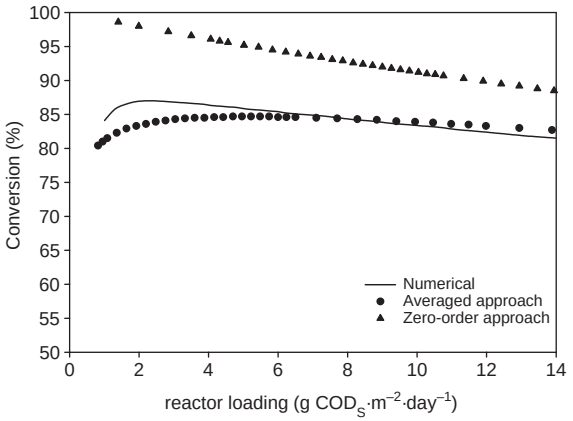

Fig. 5. Evaluation of substrate concentration in the outflow in terms of percentage conversion (%).

4. Discussion

4.1. Multi-species biofilm modeling

A set of conditions has been chosen to evaluate a biofilm consisting of autotrophs, heterotrophs and inert biomass (specified in Table 2). Stoichiometric matrix and kinetics expressions are defined in Table 1, and biological and physical parameters in Table 2. The study case described by conditions in Table 2 has been solved using the weighted average approach and also assuming square root kinetics.

4.1.1. Steady state in multi-species flat biofilms

The results obtained with the weighted average approach of the analytical solutions are presented in Table 3. Results corresponding to substrate concentrations (C_S for COD, heterotrophs; C_N for ammonium, autotrophs), fluxes in the biofilm ($J_S^{biofilm}$, $J_N^{biofilm}$ and J_{O_2} biofilm for oxygen—autotrophs and heterotrophs), biomass concentration (presented per square meter of biofilm surface) and detached biomass (also shown per square meter of biofilm surface) are detailed in Table 3. The bulk dissolved oxygen concentration has been maintained constant (simulating a dissolved oxygen control), at a value of $10\,g\,m^{-3}$.

In this case study, the main goal was to evaluate the results in a standard system, in which no substrate limitation occurred. The results regarding degradation show how both microorganisms are able to grow in the biofilm. The steady-state concentration of heterotrophs is almost 10 times higher than that of autotrophs, due to the important difference in yield of each microorganisms. It is also important to outline that the inert biomass concentration in the biofilm in steady state is twice the autotrophs concentration. For this reason, inactivation of biomass in the biofilm should always be taken into account. To maintain a biofilm thickness of $500\,\mu m$ in steady state, the detachment rate in the biofilm is $0.41\,days^{-1}$. Taking this rate, the detachment of each biomass species in the biofilm in steady state can be quantified.

4.1.1.1. Results obtained with the solution for zero-order kinetics. Although using the zero-order solution is often discarded due to the error associated for values of substrate concentration close to the affinity constant (i.e. $C_S/K_S = 1$), it is judged interesting to determine the deviation of this approach because of its simplicity. In Table 3, results computed with the zero-order approach

Table 3
Steady-state results for three different multi-species biofilms cases using weighted average, zero-order approach, AQUASIM (Reichert, 1998) and 2-D modeling (Picioreanu et al., 2003) (ND = not determined)

Variable	Units	Averaged approach	Zero-order approach	1-D Aquasim	2-D multi-species
C_S	$gCOD_S\,m^{-3}$	5.20	2.11	4.81	5.14
C_N	$gN\,m^{-3}$	1.76	0.99	1.45	1.50
$J_S^{biofilm}$	$gCOD_S\,m^{-2}\,day^{-1}$	4.96	5.58	5.04	4.95
$J_N^{biofilm}$	$gN\,m^{-2}\,day^{-1}$	0.85	1.00	0.91	0.89
J_{O_2} biofilim	$g\,m^{-2}\,day^{-1}$	6.76	7.69	6.54	6.36
b_{det}	day^{-1}	0.41	0.49	n.d.	n.d.
$C_{XH}L_f$	$gCOD\,m^{-2}$	3.86	3.96	2.13	1.81
$C_{XA}L_f$	$gCOD_X\,m^{-2}$	0.36	0.38	0.91	0.72
$C_{XI}L_f$	$gCOD_X\,m^{-2}$	0.77	0.66	1.96	2.60
$C_{XH}b_{det}$	$gCOD_X\,m^{-2}\,day^{-1}$	1.60	1.96	2.39	2.41
$C_{XA}b_{det}$	$gCOD_X\,m^{-2}\,day^{-1}$	0.15	0.19	0.09	0.11
$C_{XI}b_{det}$	$gCOD_X\,m^{-2}\,day^{-1}$	0.32	0.33	0.17	0.32
$C_{Xf}b_{det}$	$gCOD_X\,m^{-2}\,day^{-1}$	2.07	2.47	2.65	2.85

have been included. As it has been already discussed, results have relatively high deviations (relative to 2-D results), and could be only used depending on the accuracy required for the subsequent applications of these calculations. In terms of flux the averaged deviation of the zero-order solution for the three cases is 11%, whereas for the bulk concentration of substrate the deviation is much higher 36%. The magnitude of the deviation is associated to the ratio C_S/K_S, as it has been already stated in Figs. 1–5.

4.1.1.2. Comparison with 1-D (AQUASIM) results. The case study has been simulated using AQUASIM 2.0 (Reichert, 1998). To use this software the guidelines described in Wanner and Morgenroth (2004) for biofilm modeling were followed. The substrate balance equation in the biofilm is solved numerically, leading to a comparison equivalent to the one shown in Figs 1–5. Good agreement is shown between the AQUASIM solution and weighted average approach. For flux estimation an average deviation of 15% was found. For effluent substrate concentration, the average deviation is 4%.

4.1.1.3. Comparison with 2-D modeling results. A 2-D biofilm model has been included in the comparison to know the deviation of weighted average and zero-order approach from a more precise and complex biofilm modeling approach. This model has been built on previous biofilm models presented in Kreft et al. (2001) and Picioreanu et al. (1998). Biomass is distributed in discrete (spherical) particles, which push each other when growing. Solutes distribution is in a continuum field inside the planar biofilm (further detailed in Picioreanu et al., 2003). As presented in Table 3, deviation of the weighted average approach is low for the estimation of the total flux of substrates in the reactor (average deviation: 4%). For the estimation of the substrate concentration in the reactor, the average deviation is 9%. The applicability of the weighted average approach to estimate conversions is shown with this comparison.

The spatial distribution of the different biomass species in the biofilm can be estimated by means of 2-D biofilm modeling. This information cannot be obtained with the weighted averaged approach, being one of the main limitations of this methodology.

4.2. Diffusion in flocs. Apparent substrate affinity constant

Two floc types have been considered: heterotrophic and autotrophic flocs. The effect of diffusion on both flux of substrate and apparent substrate affinity constant were investigated. The kinetic parameters and physical constants assumed to compute the flux are growth rate ($\mu_{max,i}$), yield coefficient (Y_i), diffusion coefficient (D_i), and biomass concentration in the biofilm (C_{Xf}) for autotrophic and heterotrophic flocs (Tables 1 and 2).

To show the effect of floc size (or specific surface area) in the flux of substrate in a flocculated sludge, the flux times specific surface area has been normalized (using Eq. (20)) and plotted against interface and bulk substrate concentration (Fig. 6), for both systems, autotrophs and heterotrophs.

As can be observed in Fig. 6(a and b), the specific surface area of flocs has a direct influence in the diffusion process in the granular particles. When the floc diameter increases (at constant reactor biomass concentration) the relative penetration depth of substrate in the floc decreases, leading to a lower flux of

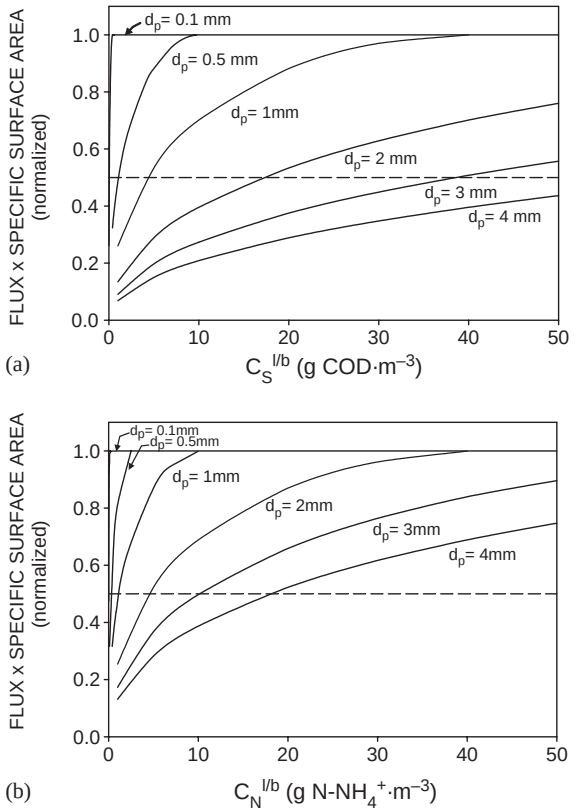

Fig. 6. Effect of particle diameter (d_p) in the flux times specific surface area in a granular or flocculated sludge: (a) heterotrophic system; (b) autotrophic NH_4^+ oxidizing system.

substrate. For a fixed substrate concentration in the bulk liquid (i.e. for a constant driving force) the higher the floc diameter, the lower the relative flux due to diffusional limitation inside the particle (decreasing the conversion in the reactor). The concentration gradients of oxygen in activated sludge flocs have been recently measured by Li and Bishop (2004). The effect of floc size on the determination of the apparent K_S values has been experimentally investigated by Chu et al. (2004).

To estimate the specific surface area (a_{sph}), spherical flocs have been considered. The flux times specific surface area ($J_i^{sph,zero}\cdots a_{sph}$) can be normalized using the term $q_S^{max}\cdots C_X\cdots\varepsilon_p$, as can be seen in the left-hand side of Eq. (20). The specific surface area (a_{sph}) can be expressed as a function of the particle radius (r_p) and particle fraction (ε_p). In that case the resulting quotient clearly is not depending on the particle fraction (ε_p), being therefore, more general:

$$\frac{J_i^{sph,zero}\,a_{sph}}{q_S^{max}\,C_X\varepsilon_p}=\frac{J_i^{sph,zero}(3/r_p)}{q_S^{max}\,C_X}. \tag{20}$$

For a value of 50% of the relative flux times specific surface area, the apparent affinity constant for these particular conditions can be determined (in Fig. 6 the intersection of the horizontal line with the different curves for different diameters). Then, it is possible to determine the apparent affinity constant using the following equation:

$$J_i^{sph,zero}a_{sph}=\left[J_i^{sph,zero}\,a_{sph}\right]^{max}\frac{C_i^{l/b}}{C_i^{l/b}+K_i^{app}}. \tag{21}$$

If

$$C_i^{l/b}=K_i^{app}\quad\text{then } J_i^{sph,zero}\,a_{sph}=\frac{\left[J_i^{sph,zero}\,a_{sph}\right]^{max}}{2}=\frac{q_S^{max}C_X}{2}. \tag{22}$$

Combining Eq. (22) with (7) and (8) it is possible to obtain an equation to estimate the apparent affinity constant:

$$K_i^{app}=1.8353\times10^{-2}\,\frac{q_S^{max}C_X r_p^2}{D_i}. \tag{23}$$

The equation has been applied to heterotrophic and autotrophic flocs using different values for biomass density. The results are shown in Fig. 7. Diffusion has a larger impact on the process (the apparent affinity constant increases) when biomass density increases.

In biofilm modeling, diffusion is included in the equations used. The kinetic parameters that should be selected are the "true" coefficients corresponding to kinetics of suspended cells. Regularly, however, the "standard" ASM coefficients (Henze et al., 1987) are used, leading to an overestimation of the concentrations in the reactor liquid. The validity of the zero-order solution is linked to the real value of the affinity constant for the particular microorganisms species. In

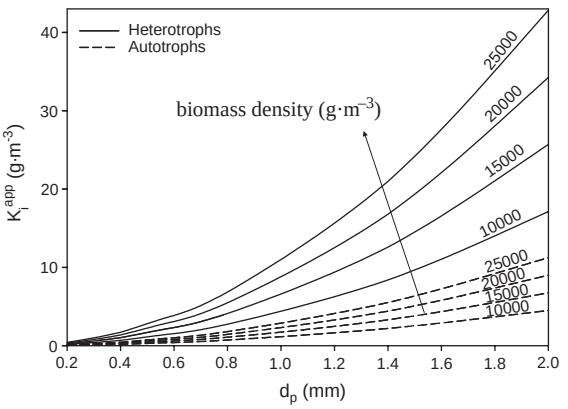

Fig. 7. Effect of floc diameter (d_p) and biomass density on the apparent affinity constant for heterotrophs and autotrophs in a flocculated activated sludge system.

wastewater modeling, effectively apparent affinity constants are used. The real values of the affinity constant are often an order of magnitude smaller. This means that the simple zero-order solution for biofilm modeling has a wider application than might be inferred from the traditional wastewater coefficients.

5. Conclusions

Using a weighted average for the zero- and first-order analytical solutions of the basic diffusion-reaction formulation provides useful information to understand, model and design steady-state biofilm reactors in a very simple way. When the interest of biofilm modeling is to determine flux and concentration of substrate in steady-state biofilm systems, the weighted average approach can be easily used with very small deviations from the more complex numerical resolution.

If the reactor substrate concentrations are high enough, the simple zero-order solution can be used. In general, for $C_S/K_S > 15$ (deviation lower than 10%) the zero-order solution can be used to compute the reactor size needed to reach a certain effluent concentration. If the objective is to describe the effluent concentration for a certain reactor, the deviation from numerical resolution is lower than 10% if $C_S/K_S > 2.5$.

The deviation of both approaches depends mainly on the particular value of the half-saturation coefficient for the biomass species in the biofilm. Differences in the half saturation coefficient between activated sludge systems and microbial values have a direct influence in the range of applicability of these two approaches. For biofilm modeling, suspended cell values for the half-saturation constant should be used not those reported for activated sludge systems.

Note: an EXCEL file can be downloaded from the Water Research website.

Appendix A. Supplementary Materials

The online version of this article contains additional supplementary data. Please visit doi:10.1016/j.watres.2004.12.020.

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