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# Denitrification kinetics in a rotating disk biofilm reactor

Rui A.R. Boaventura, Alírio E. Rodrigues \*

Laboratory of Separation and Reaction Engineering, Faculty of Engineering, University of Porto, 4099 Porto Codex, Portugal

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## Abstract

Denitrification kinetics of a synthetic substrate containing molasses, sodium nitrate,  $Na_2HPO_4 \cdot 12H_2O$ ,  $KH_2PO_4$  and tap water treated with  $Na_2SO_3$  was studied in a rotating disk biofilm reactor (RDBR).

Experiments were performed at various conditions: biofilm thickness in the range 100–1100  $\mu$ m and nitrate concentration in the feed of 5 to 50 mg N l<sup>-1</sup>. Biofilm density decreases with increasing biofilm thickness.

Most experiments were in the kinetic controlled regime or fully penetrated biofilms. The intrinsic zero-order kinetic constant was found to be  $k_0 = 7.96 \times 10^{-6}$  kg NO<sub>3</sub>-N\*kg biofilm<sup>-1</sup> s<sup>-1</sup> (at 25 °C). Some runs were in the diffusion controlled regime or partially penetrated biofilms; the effective diffusivity of nitrate in the biofilm which fitted experimental results was  $D_b = 1.5 \times 10^{-9}$  m<sup>2</sup> s<sup>-1</sup>.

The efficiency of the RDBR, considered as a CSTR, predicted by a model based on a zero-order reaction and diffusion inside the biofilm, reasonably agrees with experimental data. © 1997 Elsevier Science S.A.

Keywords: Denitrification; Kinetics; Biofilm reactors; Rotating disk reactor

#### 1. Introduction

Nitrogen compounds contained in wastewater have an important impact on the environment. Biological oxidation of such compounds leads to nitrites and nitrates as final products. Nitrates also appear in draining waters as a result of excessive use of fertilizers, or as industrial residues in chemical plants (fertilizers, paper, metal finishing, nuclear industry). The ultimate consequence of nitrates on the environment is the eutrophication of aquatic medium.

Nitrates contained in wastewater are reduced during denitrification to gaseous nitrogen through intermediate products such as nitrites and probably NO and  $NO_2$  [1]. Since denitrifying bacteria are facultative heterotrophs they need an organic carbon source to achieve metabolic processes. In most secondary effluents of wastewater treatment plants the organic carbon is insufficient and therefore a second carbon source is required, e.g. methanol.

The biological removal of nitrates from wastewater can be achieved by using suspended growth nitrification/denitrification processes, conventional fixed biofilm reactors (trickling filters or rotating biological contactors) or fluidized bed reactors [2,3]. Detailed analysis of biofilms and biofilm reactors are available in Refs. [4–7]. The scientific design of biofilm reactors requires information on denitrification kinetics. Several authors [8–10] have found that zero-order approximation is appropriate for the denitrification rate law. In practical applications the nitrate species is the limiting substrate and the zero-order approximation is justified due to the low saturation constant ( $K_s < 1$ mg NO<sub>3</sub>–N 1<sup>-1</sup>). Denitrification kinetic data can be obtained in a laboratory biofilm reactor [11]. A good review of laboratory biofilm reactors can be found in Ref. [12].

The choice of a laboratory biofilm reactor for the study of denitrification kinetics is guided by three factors: welldefined hydraulic characteristics, biofilm homogeneity and easy operation. Jansen [13] compared various biofilm reactor types, namely horizontal cylinder, sloping plane, two compartment, submerged rotating drum and rotating disk. The "horizontal cylinder" and "sloping plane" systems have the disadvantage of being distributed systems leading to nonhomogeneous conditions for growth with liquid flow in a laminar regime. The "two compartment system" developed by Williamson and McCarty [14] is an austicious one; the two compartments have different substrates separated by a biofilm artificially obtained (by filtration of a culture medium through a support). This raises the question of whether or not biofilm properties are similar to those of a naturally developed biofilm. In the submerged rotating drum, film mass transfer resistance can be eliminated by increasing the rotating speed;

<sup>\*</sup> Corresponding author.

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however, the biofilm does not grow equally in both fixed and rotating cylinders. Also one needs to empty the reactor for measurement of biofilm thickness.

The rotating disk biofilm reactor (RDBR) is a fixed cylindrical vessel in which a disk rotates in the culture medium. By adjusting the disk rotating speed the system behaves as a perfectly mixed reactor which is convenient for the analysis of results. It also provides conditions for homogeneous biofilm development [15,16]. Changes in the disk position can be made from time to time to obtain similar biofilms both sides of the disk. Biofilm thickness can be measured just by removing the disk from the solution. This system was chosen because it is simple to build and easy to operate.

The design of denitrification processes such as fluidized beds [17] and packed beds [18] can be improved by using reaction rates and diffusivities of substrates measured in simple experiments in RDBR.

The objectives of this work are:

(i) to measure denitrification kinetics in a rotating disk biofilm reactor using molasses as the carbon source for different biofilm thicknesses and feed nitrate concentrations;

(ii) to analyse the competition between reaction and diffusion in biofilms in order to obtain the zero-order kinetic constant and the effective diffusivity of the substrate inside the biofilm, accounting for the fact that biofilm density changes with biofilm thickness;

(iii) to test simple design equations for biofilms operating under diffusion controlled conditions.

#### 1.1. Model development

#### 1.1.1. Diffusion and reaction inside the biofilm

The analysis of denitrification kinetics in a biofilm is based on the following assumptions: the nitrate species is the limiting substrate, the biofilm is a homogeneous slab of thickness *L* and density  $\rho_b$  covering an inert non-porous material, liquid film mass transfer is negligible, mass transport inside the biofilm follows Fick's law of diffusion and the reaction rate is of zero order, i.e.  $r = k_o$  where  $k_o$  is the intrinsic kinetic constant referred to the biofilm mass.

The mass balance of a substrate in a biofilm element of thickness dz is:

$$D_{\rm b} \frac{{\rm d}^2 N'}{{\rm d}z^2} = k_{\rm o} \rho_{\rm b} \tag{1}$$

where z is the distance from the liquid/biofilm interface, N' is the nitrate concentration inside the biofilm and  $D_b$  is the effective diffusivity of nitrate in the biofilm. Introducing dimensionless variables for space x = z/L and concentration f = N'/N where N is the nitrate concentration at the liquid/biofilm interface, the mass balance becomes:

$$\frac{\mathrm{d}^2 f}{\mathrm{d}x^2} = \phi^2 \tag{2}$$

where the model parameter is the Thiele modulus  $\phi^2 = (k_o \rho_b L^2) / (D_b N)$ . Two situations can occur.

(i) In the case of fully penetrated biofilms (or a kinetic controlled regime), the boundary conditions associated with Eq. (2) are x=0, f=1 and x=1, df/dx=0. The dimensionless nitrate concentration profile inside the biofilm is  $f=\frac{1}{2}\phi^2x^2-\phi^2x+1$  for  $\phi<\sqrt{2}$ . The biofilm works in the kinetic controlled regime [19,20]; the biofilm effectiveness factor is  $\eta=1$ .

(ii) In the case of partially penetrated biofilms (or a diffusion controlled regime) the boundary conditions for the Eq. (2) are now x = 0, f = 1 and  $x = x^*$ , f = 0 and df/dx = 0 where  $x^*$  is the reduced distance inside the biofilm at which the dimensionless nitrate concentration is zero. The dimensionless nitrate concentration profile inside the biofilm, valid for  $\phi > \sqrt{2}$ , is given by  $f = \frac{1}{2}\phi^2 x^2 - \sqrt{2}\phi x + 1$ . The biofilm effectiveness factor is  $\eta = x^* = \sqrt{2}/\phi$ .

The observed nitrate removal rates  $r_{w,obs}$  (referred to the biofilm mass) can be calculated from the diffusion flux at the biofilm surface or simply  $r_{w,obs} = \eta k_{op}$  leading to: (i) a fully penetrated biofilm ( $\phi < \sqrt{2}, \eta = 1$ )

$$r_{\rm w,obs} = k_{\rm o} \tag{3a}$$

(ii) Partially penetrated biofilm ( $\phi > \sqrt{2}$ ,  $\eta = \sqrt{2}/\phi$ )

$$r_{\rm w,obs} = \sqrt{\frac{2k_o D_b}{\rho_b L^2}} N^{1/2}$$
(3b)

Eq. (3) shows that in the diffusional regime the "apparent" reaction order is 1/2 as we know from the competition of an intrinsic zero-order reaction and diffusion [21]. The "apparent" kinetic constant of a 1/2-order reaction is

$$k_{1/2} = \sqrt{\frac{2k_{\rm o}D_{\rm b}}{\rho_{\rm b}L^2}}$$

expressed in (kg nitrate removed)<sup>1/2</sup> \* (kg biofilm)<sup>-1</sup> s<sup>-1</sup>  $m^{3/2}$ .

#### 1.1.2. Rotating disk biofilm reactor

The rotating disk biofilm reactor is considered as a CSTR; the mass balance for the substrate over the reactor in steady state is:

$$QN_{\rm in} = QN_{\rm out} + r_{\rm w,obs}(N_{\rm out})\rho_{\rm b}AL$$
<sup>(4)</sup>

The observed nitrate removal rate is then:

$$r_{\rm w,obs} = \frac{Q(N_{\rm in} - N_{\rm out})}{\rho_{\rm b}AL}$$
(5)

where A is the total disk area (both sides), Q is the flowrate, and  $N_{in}$ ,  $N_{out}$  are nitrate concentrations in the feed and at the outlet, respectively. It should be noted that the nitrate removal rate referred to the biofilm area is  $r_{a,obs} = r_{w,obs} \rho_b L$ .

#### 1.1.3. Efficiency of the rotating disk biofilm reactor

The conversion of nitrate species or efficiency of a perfectly mixed biofilm reactor, defined as  $E_a = 1 - (N_{out}/N_{in})$ , can be obtained by combining Eqs. (5) and (3) for fully penetrated biofilms or Eqs. (5) and (3) in the case of partially penetrated biofilms leading to [22]:

$$E_{\rm a} = N_{\rm r} = \frac{k_{\rm o} \rho_{\rm b} \tau}{N_{\rm in}}$$
 (kinetic controlled regime) (6a)

and

$$E_{\rm a} = \sqrt{\alpha(\alpha + 2)} - \alpha$$
 (diffusion controlled regime) (6b)

with  $\alpha = N_r N_b$  where  $N_r$  is the number of reaction units or Damkholer number,  $N_b = (D_b \tau) / L^2$  is the number of biofilm diffusion units and  $\tau$  is the ratio between biofilm volume  $V_b$ and flowrate Q.

#### 2. Experimental

The rotating disk biofilm reactor used in this work was built according to Ref. [2]. It is a cylindrical reservoir made of plexiglass. The shaft holds a plexiglass disk which is the biofilm support. In order to easily measure biofilm thickness both sides of the disk have slabs which can be taken out.

The synthetic substrate is fed through a tube located at the disk level; the outlet level is at 1/3 of the height. Nitrogen is dispersed near the reactor bottom in order to keep an anoxic atmosphere above the liquid phase. The system was covered with an aluminium sheet to avoid algae development.

The reactor characteristics are summarized in Table 1. In further analysis it is considered as a CSTR. This is supported by tracer experiments done using KCl as tracer. The experimental set-up shown in Fig. 1 includes the RDBR, a thermostated bath, reservoirs and pumps for liquid circulation. The synthetic substrate is made of molasses, sodium nitrate,

Table 1

Characteristics of the rotating disk biofilm reactor

Total volume (cm <sup>3</sup> )	5954	
Useful volume (cm <sup>3</sup> )	2000	
Internal diameter (cm)	19	
Useful height (cm)	7	
Disk area (one side) (cm <sup>2</sup> )	153.4	
Disk thickness (cm)	0.8	



Fig. 1. Experimental set-up for kinetic studies in a rotating disk biofilm reactor (RDBR): R, RDBR; M, stirrer; T, thermostated bath; P, pumps; T, reservoirs.

 Table 2

 Compositions of synthetic substrate and molasses

Synthetic substrate <sup>a</sup>	
$NO_3 - N (mg l^{-1})$	20
molasses (mg $1^{-1}$ )	800
$Na_2HPO_4 \cdot 12H_2O-P (mg l^{-1})$	100
$KH_2PO_4 - P (mg 1^{-1})$	100
Inoculum (ml $l^{-1}$ )	2
Molasses	
COD (mg $g^{-1}$ of molasses)	790
TOC (mg $g^{-1}$ of molasses)	262.5
$NH_4-N (mg g^{-1} of molasses)$	6.3
soluble P (mg $g^{-1}$ of molasses)	0.12
рН	7.5
COD/TOC	3
dry matter	75%
sucrose	59% of dry matter
ash	12.5% of dry matter

<sup>a</sup> In tap water previously dechlorinated and deoxygenated.

 $Na_2HPO_4 \cdot 12H_2O$ ,  $KH_2PO_4$  and tap water deoxygenated with  $Na_2SO_3$ . Molasses (carbon source) were added in order to obtain a COD/NO<sub>3</sub>-N ratio of 40; in such conditions nitrate is the limiting reactant.

Typical compositions of the synthetic substrate and molasses are presented in Table 2. The inoculum was a secondary effluent of a domestic sewage treatment plant in which microorganisms were previously adapted to a culture medium of molasses, sodium nitrate and phosphates.

The reactor is initially filled with synthetic substrate and nitrogen fed through the diffuser. The operation is done in closed system with a disk speed of 40 rpm. After 72 h adhesion of biomass to the disk is already achieved and the operation is changed to open mode with feed flowrate of 50 ml min<sup>-1</sup>. Five days are enough to obtain uniform biofilms. The disk speed is then increased until 100–120 rpm. Biofilm thickness can reach 1000–1200  $\mu$ m before sloughing off the biofilm. When this happens a "new" biofilm of 100–200  $\mu$ m thickness is already adherent to the disk.

Fig. 2(a), 2(b) and 2(c) show the biofilm development and its sloughing off. Nitrate was determined using an ion specific electrode. Further details concerning analytical methods can be found elsewhere [23].

#### 3. Results and discussion

All kinetic runs were carried out at 25 °C at flowrates of the order of 50 ml min<sup>-1</sup> (or space times around 40 min), nitrate concentration in the feed in the range of 5 to 50 mg  $1^{-1}$ , biofilm thickness between 100 and 1100  $\mu$ m, pH in the range 7.02 to 7.86 and total organic carbon/nitrate ratio TOC/NO<sub>3</sub>-N=9.3-14.

Table 3 shows all data (27 runs) grouped in classes A–E according to the biofilm thickness. The observed removal rate of nitrate was calculated from Eq. (5).



Fig. 2. Biofilm development: (a) biofilm thickness, 200  $\mu$ m, (b) biofilm thickness, 1200  $\mu$ m, (c) biofilm detachment.

## 3.1. Biofilm density

The biofilm thickness was measured at the removable slabs of the disk using a microscope equipped with a stage micrometer and following the procedure described by Ref. [2]. From the measurement of biofilm thickness, L (averaged over seven measures) and volatile solids, VS (difference between the mass of dry biofilm at 105 °C and the mass of biofilm after calcination at 505 °C), the wet biofilm density  $\rho_{\rm b}$  (kg VS m<sup>3</sup> of wet biofilm<sup>-1</sup>) was calculated. Experimental

 Table 3

 Nitrate removal rates in a rotating disk biofilm reactor: experimental data

Run	Biofilm thickness L (μm)	$\frac{\rho_b}{(\text{kg m}^{-3})}$	FlowrateQ (ml min <sup>-1</sup> )	Feed nitrate concentration $N_{in}$ (mg l <sup>-1</sup> )	Outlet nitrate concentration $N_{out}$ (mg l <sup>-1</sup> )	Observed nitrate removal rate, $r_{a,obs} \times 10^8$ (kg m <sup>-2</sup> s <sup>-1</sup> )	Observed nitrate removal rate, $r_{w,obs} \times 10^{6}$ (kg kg <sup>-1</sup> s <sup>-1</sup> )
A.15 <sup>a</sup>	110	90.6	47	5.1	2.3	7.15	7.17
A.12	100	91.9	47	9.3	6.4	7.40	8.06
A.13	100	91.9	49	13.9	11.0	7.72	8.40
A.16	120	89.4	48	29.5	26.0	9.12	8.50
A.17	120	89.4	48	29.8	27.0	7.30	6.81
A.14	100	91.9	46	40.1	37.0	7.34	7.99
B.21 ª	210	78.2	47	9.5	5.2	10.97	6.68
B.19	200	79.4	53	19.2	15.0	12.09	7.61
<b>B.20</b>	200	79.4	53	24.5	20.0	12.95	8.15
<b>B</b> .22	214	77.7	46	48.1	43.5	11.49	6.91
<b>B</b> .18	191	80.5	52	50.4	46.0	12.42	8.07
B.23	214	77.7	46	53.0	48.0	12.49	7.51
C.4 <sup>a</sup>	363	59.1	47	14.6	8.7	15.06	7.02
C.6	415	52.6	46	17.6	11.2	15.99	7.32
C.5	363	59.1	47	18.8	12.8	15.31	7.13
C.1	497	42.4	48	22.8	16.5	16.42	7.78
C.2	497	42.4	48	42.0	35.5	16.94	8.03
C.3	510	40.8	50	46.5	41.0	14.93	7.17
C.7	445	48.9	47	47.4	41.0	16.33	7.50
D.11 <sup>a</sup>	799	26.9	47	12.6	7.1	14.04	6.53
D.8	721	26.9	47	16.9	10.2	17.10	8.82
D.9	721	26.9	47	19.7	13.3	16.31	8.41
D.10	754	26.9	47	33.5	26.4	18.14	8.94
E.24 <sup>a</sup>	895	26.9	48	11.2	6.1	13.29	5.52
E.28 <sup>a</sup>	1100	26.9	47	21.3	14.3	17.86	6.04
E.26	1000	26.9	47	26.6	18.7	20.16	7.49
E.29	1100	26.9	46	36.0	26.5	23.73	8.02
E.25	929	26.9	46	36.8	28.5	20.73	8.30
E.27	1000	26.9	46	38.8	30.0	21.98	8.17

Temperature T = 25 °C; area of Biofilm (both sides)  $A = 3.069 \times 10^{-2}$  m<sup>2</sup>. <sup>a</sup> Runs with partially penetrated biofilms (diffusion controlled regime).

results of the wet density of the biofilm  $\rho_b$  as a function of the biofilm thickness *L* are shown in Fig. 3. The wet density of the biofilm  $\rho_b$  linearly decreases with biofilm thickness until  $L = 622 \ \mu m$  and then remains constant, i.e.  $\rho_b = 104.3$ -



Fig. 3. Biofilm density  $\rho_{\rm b}$  as a function of biofilm thickness L.

0.12446L ( $\mu$ m) for 0 < L < 622  $\mu$ m and  $\rho_{\rm b} = 26.9$  kg VS m<sup>3</sup> of wet biofilm<sup>-1</sup> for L > 622  $\mu$ m.

#### 3.2. Stoichiometry of the denitrification reaction

Fig. 4 shows experimental data for the nitrate removal in the reactor  $\Delta NO_3$ -N (mg l<sup>-1</sup>) as a function of the carbon consumed  $\Delta TOC$  (mg l<sup>-1</sup>). A linear fitting leads to  $\Delta TOC / \Delta NO_3$ -N=2.52. This result agrees with data obtained in a batch operation [23]. In all experiments a TOC/N–NO<sub>3</sub> ratio of 9.3 to 14 in the feed was used to guarantee that nitrate was the limiting substrate.

The stoichiometry of the denitrification process (neglecting assimilation) has been considered by several authors. When methanol is the carbon source the denitrification reaction is:

$$NO_{3}^{-} + \frac{5}{6}CH_{3}OH \rightarrow \frac{1}{2}N_{2} + \frac{5}{6}CO_{2} + \frac{7}{6}H_{2}O$$

and theoretically the stoichiometric ratio  $CH_3OH/NO_3-N$  is 1.9. However, the stoichiometric ratio should be higher due



Fig. 4. Nitrate removal  $\Delta NO_3$ -N as a function of total organic carbon consumed  $\Delta TOC$  in a RDBR.



Fig. 5. Observed denitrification reaction rate as a function of the outlet nitrate concentration N in a RDBR: model based on zero-order reaction and diffusion inside the biofilm (a)  $r_{a,obs}$  versus N, (b)  $r_{w,obs}$  versus N.

to the assimilatory reaction [24]. Assuming sucrose as the only carbon source present in molasses, the denitrification reaction will be written as:

$$C_{12}H_{22}O_{11} + 48NO_3^- \rightarrow 24N_2 + 60CO_2 + 48OH^-$$

The stoichiometric ratio sucrose/NO<sub>3</sub>-N is then 2.54. Since bacteria growth needs a complementary quantity of molasses ( $\approx 30\%$ ) and the sucrose content of molasses is 44.3% (Table 2) we conclude the ratio molasses/NO<sub>3</sub>-N should be of the order 8.1 or a TOC/NO<sub>3</sub>-N ratio of 2.1.

#### 3.3. Intrinsic zero-order kinetic constant

The experimental results from Table 3 are plotted in Fig. 5(a) and 5(b) in terms of the observed removal rate of nitrate  $r_{w,obs}$  (kg NO<sub>3</sub>-N removed \*kg biofilm<sup>-1</sup> s<sup>-1</sup>) or  $r_{a,obs}$  (kg m<sup>-2</sup> s<sup>-1</sup>) as a function of the outlet nitrate concentration N (kg m<sup>-3</sup>), respectively.

From plateau values (runs with fully penetrated biofilms) in the plot  $r_{w,obs}$  vs. N we obtain the intrinsic kinetic constant  $k_o$ . Experiments were grouped according to the average biofilm thickness and the average intrinsic kinetic constant is

Table 4

Measured values of the intrinsic zero-order kinetic constant  $k_0$  (experiments under kinetic controlled regime)

Run	Average biofilm thickness $L \times 10^6$ (m)	Average kinetic constant $k_0 \times 10^6$ (kg kg <sup>-1</sup> s <sup>-1</sup> )
A. 12–14, 16, 17	108	7.95
B. 18–20, 22, 23	205	7.65
C. 1-3, 5-7	441	7.49
D. 8–10	749	8.72
E. 25, 27, 29	1004	8.00

Temperature T = 25 °C; total biofilm area  $A = 3.068 \times 10^{-2}$  m<sup>2</sup>.

Table 5

Comparison of observed zero-order kinetic constants with those obtained by Jansen and Kristensen [25]

This work $(T = 25 ^{\circ}\mathrm{C})$		Jansen and Kristensen [25]		
Biofilm thickness $L \times 10^6$ (m)	$\frac{\bar{k_o}}{(g m^{-3} s^{-1})}$	Biofilm thickness $L \times 10^6$ (m)	$\bar{k_o}$ (g m <sup>-3</sup> s <sup>-1</sup> )	
108	0.72	60	0.64	
205	0.60	200	0.35	
441	0.37	500	0.26	
749	0.23	1000	0.21	
1004	0.22			



Fig. 6. (a) Efficiency of a RDBR,  $E_a$  as a function of the number of reaction units,  $N_r$ : model predictions with Eq. (6); biofilm working in kinetic controlled regime. (b) Efficiency of a RDBR,  $E_a$  as a function of  $\alpha$ : model predictions with Eq. (6); biofilm in the diffusion-controlled regime.

 $k_0 = 7.96 \times 10^{-6}$  kg NO<sub>3</sub>-N \* kg VS<sup>-1</sup> s<sup>-1</sup> calculated from data reported in Table 4.

Table 5 compares the values of the kinetic constant referred to the biofilm volume  $\bar{k}_0 = k_0 \rho_b$  (g nitrate removed m<sup>3</sup> biofilm volume<sup>-1</sup> s<sup>-1</sup>) with those obtained by Ref. [25]. It is observed that  $\bar{k}_0$  decreases from 0.73 g m<sup>-3</sup> s<sup>-1</sup> to 0.22 g m<sup>-3</sup> s<sup>-1</sup> when biofilm thickness increases from 108 µm to 1004 µm. This is simply a consequence of the fact that thicker biofilms have lower density.

#### 3.4. Effective diffusivity of nitrate inside the biofilm

For each biofilm thickness the rate of nitrate removal is constant above a critical nitrate concentration corresponding to the situation of a fully penetrated biofilm (kinetic controlled regime). Below that critical value, experimental points are fitted by a parabola  $r_{w,obs} = \sqrt{(2k_oD_b)/(\rho_{max}L_e^2)} \times N^{1/2}$  or  $r_{a,obs} = \sqrt{2k_o\rho_{max}D_b}N^{1/2}$  corresponding to the partially penetrated biofilm (or diffusion controlled regime). In these equations  $L_e$  is the thickness of an equivalent biofilm with density  $\rho_{max} = 104.3$  kg VS m<sup>3</sup> of wet biofilm<sup>-1</sup>, i.e.  $L_e = L\rho_b/\rho_{max}$ . In fact, biofilms are heterogeneous and thicker biofilms clearly show nitrogen bubbles entrapped near the disk surface.

Experimental and model results are compared in Fig. 5(b) for an effective diffusivity of nitrate inside the biofilm  $D_{\rm b} = 1.5 \times 10^{-9} \, {\rm m}^2 \, {\rm s}^{-1}$ .

The apparent kinetic constant for partially penetrated biofilms  $k_{1/2} = \sqrt{2k_o\rho_{max}D_b}$ , expressed as  $g^{1/2} \text{ m}^{-1/2} \text{ s}^{-1}$ , has to be compared with data from other authors. Jansen and Kristensen [25] reported values in the range  $1.0 \times 10^{-5}$  to  $4.3 \times 10^{-5} \text{ g}^{1/2} \text{ m}^{-1/2} \text{ s}^{-1}$ . Harremöes [26] reviewed denitrification data in packed beds operating at temperatures in the range 6-27 °C leading to  $k_{1/2}$  in the range  $0.05 \times 10^{-5}$  to  $2.5 \times 10^{-5} \text{ g}^{1/2} \text{ m}^{-1/2} \text{ s}^{-1}$ . Watanabe and Ishiguro [27] using a biodisk obtained  $k_{1/2} = 3.6 \times 10^{-5} \text{ g}^{1/2} \text{ m}^{-1/2} \text{ s}^{-1}$ . The value found in this work  $k_{1/2} = 5.0 \times 10^{-5} \text{ g}^{1/2} \text{ m}^{-1/2} \text{ s}^{-1}$  is to be compared with those of Ref. [25]. The values measured in packed beds are lower; however, in packed beds bubbles can reduce the biofilm surface in contact with the substrate and consequently the observed nitrate removal is lower.

#### 3.5. Reactor design

Once the basic quantities  $k_o$  and  $D_b$  have been measured one can predict the efficiency of a perfectly mixed biofilm reactor or plug flow biofilm reactor. According to Ref. [22] the efficiency of the RDBR, considered as a CSTR, is given by Eqs. 6(a) and (b) for situations of fully and partially penetrated biofilm, respectively.

Fig. 6(a) shows the reactor efficiency  $E_a = 1 - (N_{out}/N_{in})$  as a function of the number of reaction units (or Damkholer number)  $N_r$ . Most runs are in the kinetic controlled regime and follow a straight line with slope 1 as predicted by the design equation  $E_a = N_r$ . It can be seen that some runs (A15, B21, C4, D11, E24 and E28) are in the diffusion controlled regime. Table 6 reports data for such runs. The Damkholer number  $N_r$  is in the range 0.43 to 0.66 and the number of biofilm diffusion units based on the equivalent

Table 6

Efficiency of a perfectly mixed biofilm reactor for partially penetrated biofilms (diffusion controlled regime)

Run	Reactor efficiency E <sub>a</sub> (exp.)	Equivalent thickness (µm) L <sub>e</sub>	Number of reaction units N <sub>r</sub>	Number of biofilm diffusion units $N_{\rm be} = N_{\rm be} = D_{\rm b}A/QL_{\rm e}$	α	Thiele modulus $\phi$	Reactor efficiency E <sub>a</sub> (model)
A 15	0.55	96	0.61	0.62	0.378	1.48	0.57
B 21	0.45	157	0.54	0.37	0.200	1.62	0.46
C.4	0.40	206	0.46	0.29	0.133	1.64	0.40
DII	0.44	206	0.53	0.29	0.154	1.82	0.42
E 24	0.46	231	0.66	0.25	0.165	2.20	0.43
E.28	0.33	284	0.43	0.21	0.090	1.77	0.34

thickness  $N_{\rm be}$  is in the range 0.21 to 0.62. Thiele modulus can be easily calculated since  $\phi^2 = (N_r/N_{\rm be})/(N/N_{\rm in})$  leading to values in the range 1.48 to 2.20. Fig. 6(b) shows  $E_{\rm a}$  as a function of  $\alpha$ ; experimental points agree with model calculations. In fact, for a perfectly mixed reactor with partially penetrated biofilms or diffusion controlled regime the design equation predicts a universal curve for the efficiency  $E_{\rm a}$  as a function of  $\alpha$ .

#### 4. Conclusions

The rotating disk biofilm reactor (RDBR) is a convenient tool for understanding biofilm development, to distinguish different working regimes of biofilms (fully penetrated biofilms and partially penetrated biofilms) and to analyse the influence of different carbon sources on denitrification processes. Biofilms with different thickness have been grown; biofilm density decreases as the thickness increases. Denitrification kinetics obtained from RDBR experiments follows a zero-order law; the intrinsic kinetic constant as well as the nitrate diffusivity in the biofilm were measured. These data coupled with batch studies (which provide information on the effect of pH, nutrients, etc.) have been used to analyse the operation of a biological fluidized bed reactor for water denitrification [28,29].

## 5. Notation

Α	biofilm	surface	area,	m²
A	01011111	surface	area,	111

- $D_{\rm b}$  nitrate diffusivity inside the biofilm, m<sup>2</sup> s<sup>-1</sup>
- $E_{\rm a}$  reactor efficiency or conversion, dimensionless
- f dimensionless nitrate concentration inside the biofilm (=N'/N)
- $k_{o}$  zero-order kinetic constant, kg nitrate removed \* kg biofilm<sup>-1</sup> s<sup>-1</sup>
- $\vec{k}_{o}$  zero-order kinetic constant based on the biofilm volume, kg nitrate removed \* m<sup>3</sup> biofilm<sup>-1</sup> s<sup>-1</sup>
- $k_{1/2}$  apparent half-order kinetic constant, kg nitrate removed  $^{1/2}$  m<sup>-1/2</sup> s<sup>-1</sup>
- *L* biofilm thickness, m
- $L_{\rm e}$  thickness of the equivalent biofilm with density  $\rho_{\rm max}$ , m
- N nitrate concentration at the biofilm surface, kg  $m^{-3}$
- N' nitrate concentration inside the biofilm, kg m<sup>-3</sup>
- $N_{\rm r}$  number of reaction units ( =  $k_{\rm o}\rho_{\rm b}\tau/N_{\rm in}$ ), dimensionless
- $N_{\rm b}$  number of biofilm diffusion units ( =  $D_{\rm b}\tau/L^2$ ), dimensionless
- $N_{be}$  number of biofilm diffusion units based on the equivalent thickness (= $D_bA/QL_e$ ), dimensionless Q feed flowrate, m<sup>3</sup>s<sup>-1</sup>
- *r* intrinsic denitrification reaction rate, kg nitrate \* kg biofilm<sup>-1</sup> s<sup>-1</sup>

- $r_{a,obs}$  observed denitrification reaction rate, kg nitrate \* m<sup>2</sup> biofilm<sup>-1</sup> s<sup>-1</sup>
- $r_{\rm w,obs}$  observed denitrification reaction rate, kg nitrate \* kg biofilm<sup>-1</sup> s<sup>-1</sup>
- $V_{\rm b}$  biofilm volume, m<sup>3</sup>
- x dimensionless space coordinate inside the biofilm (=z/L)
- x\* distance inside the biofilm at which both concentration and its derivative are zero
- z space coordinate inside the biofilm, m

## Subscripts

1 <b>n</b>	reactor	inlet

out reactor outlet

## Greek symbols

- $\alpha$  parameter in Eq. (6) (= $N_r N_b$ )
- $\phi$  Thiele modulus (= $L\sqrt{K_{o}\rho_{b}/D_{b}N}$ )
- $\rho_{\rm b}$  biofilm density
- $\rho_{\rm max}$  density of the "equivalent" biofilm
- $\eta$  biofilm effectiveness factor
- $\tau$  ratio between biofilm volume and flowrate (=  $V_{\rm b}/Q$ ), m<sup>3</sup> biofilm m<sup>3</sup> liquid<sup>-1</sup> s

## References

- E. Renner, G. Becker, Production of nitric oxides and nitrous oxide during denitrification by Loryebacterium nephridis, J. Bacteriol. 101 (1970) 821.
- [2] L. Mulcahy, E. La Motta, Mathematical Model of the Fluidized Bed Biofilm Recator, Report E-59-78-2, Department of Civil Engineering, University of Massachussets, 1978.
- [3] W. Shieh, L. Mulcahy, E. La Motta, Fluidized bed biofilm reactor effectiveness factor expressions, Trans. IChE 59 (1981) 129.
- [4] W. Characklis, K. Marshall, Biofilms, Wiley, New York, 1990.
- [5] J. Bernard, Technical Advances in Biofilm Reactors, Wat. Sci. Tech. 22 (1/2) (1990).
- [6] J. Bryers, W. Characklis, Biofilm accumulation and activity: a process analysis, in: L. Melo, T. Bott, M. Fletcher, B. Capdeville (eds.), Biofilms: Science and Technology, Kluwer, Dordrecht, 1992.
- [7] L. Melo, T. Bott, M. Fletcher, B. Capdeville, Biofilms: Science and Technology, Kluwer, Dordrecht, 1992.
- [8] R. Dawson, K. Murphy, The temperature dependency of biological denitrification, Wat. Res. 6 (1973) 71.
- [9] P. Sutton, K. Murphy, R. Dawson, Continuous Biological Denitrification of Wastewater, Environment Canada, Env. Prot. Ser. Tech. Div., Report. EPS 4-WP-74-6, 1974.
- [10] M. Christensen, P. Harremöes, Nitrification and denitrification in wastewater treatement, in: R. Mitchell (ed.), Water Pollution Technology, Vol. 2, Wiley, New York, 1978.
- [11] G. Kristensen, J. Jansen, Fixed film kinetics description of laboratory equipment, Report 80-58, Dept. of Sanitary Engineering, Tech. Univ. Denmark, 1980.
- [12] W. Characklis, Laboratory biofilm reactors, in: W. Characklis, K. Marshall (eds.), Biofilms, Wiley, New York, 1990.
- [13] J. La Cour Jansen, Fixed kinetics removal of soluble substrates, Ph.D. Thesis, Technical University of Denmark, 1983.
- [14] K. Williamson, P.L. Mc Carty, Verification studies of the biofilm model for bacterial substrate utilization, JWPCF 48 (2) (1976) 281.

- [15] W. Characklis, Fouling biofilm development: a process analysis, Biotechnol. Bioeng, 23 (1981) 1923.
- [16] J. Bryers, W. Characklis, Process governing biofilm formation, Biotechnol. Bioeng. 124 (1982) 2451.
- [17] L. Mulcahy, W. Shieh, E. La Motta, Simplified mathematical model for a fluidized bed biofilm reactor, AlChE 77 (209) (1981) 273.
- [18] A. Parker, L. Sikora, R. Hughes, Denitrification kinetics in packed beds, AIChEJ 22 (5) (1976) 851.
- [19] B. Atkinson, Biochemical Reactors, Pion Limited, London, 1974.
- [20] P. Harremöes, Biofilm kinetics, in: R. Mitchell (ed.), Water Pollution Microbiology, Wiley, New York, 1978.
- [21] R. Aris, The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts, Vol. I — The Theory of the Steady State, Clarendon Press, Oxford, 1975.
- [22] A. Rodrigues, A. Grasmick, S. Elmaleh, Modelling of Biofilm Reactors, Chem. Eng. J. 27 (2) (1983) B39.
- [23] R. Boaventura, Biological Denitrification in Fixed Biofilm Reactors, Ph.D. Thesis, University of Porto, 1986.

- [24] J. Jeris, R., Owens, R. Hickey, F. Flood, Biological fluidized bed treatement for BOD and nitrogen removal, JWPCF 49 (1977) 816.
- [25] J. La Cour Jansen, G. Kristensen, Fixed film kinetics denitrification in fixed films, Report 80-59, Technical University of Denmark, 1980.
- [26] P. Harremöes, Half-order reactions in biofilm and filter kinetics, Vatten 2 (1977) 22.
- [27] Y. Watanabe, M. Ishiguro, 1978, Denitrification kinetics in a submerged rotating biological disk unit, Prog. Wat. Technol. 10 (5/ 6) (1978) 187.
- [28] R. Boaventura, A. Rodrigues, Consecutive reactions in fluidized bed biological reactors: modeling and experimental study of wastewater denitrification, Chem. Eng. Sci. 43 (10) (1986) 2715.
- [29] I. Coelhoso, R. Boaventura, A. Rodrigues, Biofilm reactors: An experimental and modeling study of wastewater denitrification in fluidized-bed reactors of activated carbon particles, Biotechnol. Bioeng. 40 (1992) 625–633.