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Modelling of the Nitrifying compartment of MELiSSA

Numerical treatment and simulations

- Updates of the previous (TN 27.2) model
- Numerical treatment of the biofilm transfer
- Identification of RTD parameters
- Sensitivity analysis
- Simulation of transient behaviours

TECHNICAL NOTE 27.3

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Content

T.N. 27.3: Modelling the nitrifying compartment
Numerical treatment and simulations

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Introduction

This technical note is the continuation of the numerical treatment of the nitrifying model presented in TN 27.1, and of the simulations of the autotrophic nitrifying process.

In the first part, the changes from the previous model (TN 27.2) are presented.

In a second part, the sensitivity of the model to the biological model parameters is studied.

In the third part, a first estimation of the hydrodynamic parameters is realised from the UAB RTD data. The influence of these parameters is taken into account in the simulation of transient behaviour of autotrophic nitrifying process in response to various perturbations (oxygen shutdown, liquid flow rates variations, NH_3 input concentration steps)

I - Updating of the nitrifying model

Two elements were added to the previous nitrifying model, stated in TN 27.2:

1- A value for the inhibitory constant of NO_3^- and NO_2^- is introduced in the biological kinetics of *Nitrobacter sp.*

2- A model for the biofilm concentration profile was build

1.1 - Inhibitory compounds

At certain concentrations, the substrates or the products of the nitrification act as inhibitors. These inhibitory effects have been detailed in TN 27.1

The biological kinetic model proposed in TN 27.1 for the autotrophic nitrification, includes an inhibitory factor (K_I) defined as:

$$K_{I-k} = 1 + \frac{C_k}{I_k}$$

where C_k is the concentration of compound k and I_k is the inhibitory constant of compound k. The specific growth rate of the micro-organism is written:

$$\mu = \mu_{max} \prod_k \frac{C_k}{(Ks_k + C_k)} \frac{1}{K_{I-k}}$$

These expression is based upon the assumption that the inhibition is a non competitive inhibition.

The inhibitory compounds in autotrophic nitrification can be N-compounds (NH_3, NO_2^- and NO_3^-) and oxygen. An overview of the inhibitory effects of N-compounds on nitrification was given in TN 27.1, as reported in the table of appendix D.

Oxygen is only inhibitory at high partial pressure (pure oxygen), thus its inhibitory effect is not taken into account in our model.

For *Nitrosomonas europea*, Hunik et al. (1994) set the K_{I-k} values to 1, assuming the inhibitory effect of NO_2^- NO_3^- and NH_3 can be neglected. By studying the effects of high concentrations of product (HNO_2), substrate (NH_4^+) and salts (NaCl, KCl, $NaNO_3$, $NaNO_2$) Hunik et al. (1993) observed a severe inhibition of *N. europea* activity at increased concentrations. Because there was no distinctions between the effects of salts, product or substrates, they concluded to an osmotic pressure effect due to high concentrations rather than a substrate inhibition. By studying the combined effect of NO_2^- and pH, they suggested, as Boon and Laudelout (1962) for *N. agilis* that the undissociated form of NO_2^- (HNO_2) is responsible for the toxic effect. This toxic effect must not be confused with the osmotic pressure effect due to high salts concentrations.

A relation is given by Hunik et al. (1993) for the effect of salts concentration on nitrification activity:

$$\frac{V}{V_m} = 0.994 - 0.00187.[\text{Salt concentration}]$$

where Vm is the O_2 consumed/s.m^3 (V_m=3250 µmol/s.m^3) and the salts concentration is in mmol/l.

As for *Nitrosomonas*, Hunik et al. (1993b) have studied the effect of salts concentration and the inhibitory effects of ammonium, nitrite and nitrate on *Nitrobacter agilis*.

The relation established for the representation of the osmotic pressure effects (Na^+, K^+,Cl^- ,SO_4^{2-}, acetate) on activity is:

$$\frac{V}{V_m} = 1.04 - 0.00088.[\text{Salt concentration}]$$

where Vm is the O_2 consumed/s.m^3 (V_m=600 µmol/s.m^3) and the salts concentration is in mmol/l.

The toxic (inhibitory) effect of HNO_2 has been mesured at pH values lower than 8 (because with an acid base dissociation constant of 3.98 10^{-4} mol/l, HNO_2 can not be detected at pH 8). The average value proposed by Hunik et al. (1993b) was 14 µmol HNO_2 /l. Even if in the pH range of 6.5 - 8.5 HNO_3 is completely dissociated, the inhibition of Nitrobacter by NO_3^- is pH dependent. The inhibitions reported by Hunik et al (1993b) on the activity of *N. agilis* are small at pH 7.5 and 8.5 for ammonium and at pH 8.5 for nitrate.

For *Nitrobacter*, Hunik et al. (1994) give inhibitory constants for a non competitive model:

I^{Nb}_{NO2-} = 0.159 mol/l (calculated from a mean value of 14 µmol HNO_2/l of toxicity for HNO_2 at pH 7.4)

I^{Nb}_{NO3-} = 0.188 mol/l (mean value at pH 7.4)

These values represent the concentration at which the specific growth rate is the half of its maximum assuming that there is no limitations or other inhibitions. At pH 8, using the acid base dissociation constant of nitrite (3.98 10^{-4} mol/l), we have I^{Nb}_{NO2-}=0.557 mol/l.

HNO_3 is a strong acid and even if Hunik et al. (1993b) have its inhibitory effect to be pH dependent, the constant given at pH 7.4 is teh same we will use at our pH 8.

It can be remarked that for the fixed bed reactor, Forler (1992) reports for Nitrobacter a 50% inhibition at pH 8 around 16 mg/l of N-NO_2^- (i.e 1.14 mmol/l NO_2^-).

A simulation of the inhibition by NO_3^- has been made in the standard conditions (listed in appendix A and B) with an addition of 0.150 mol/l of HNO_3 in the liquid input. At steady state the nitrifiying efficiency is reduced to 90.9% (95.7% with no inhibition), the mean biomass concentration is quite unchanged, and the *Nitrobacter* population is very little affected (29% of the total population instead of the 29.5% with no inhibition). The nitrite concentration at steady state is doubled with the inhibition (3 10^{-3} mol/l).

Considering the high concentration of NO_2^- needed to simulate an inhibition by HNO_2, the simulation has not been performed.

1.2 - Biofilm model

The problem of the mass transfer limitations in biofilms was studied in TN 27.1. In the first simulations of autotrophic nitrification (TN 27.2), the biofilm limitation was not taken into account. The results of these simulations showed that the biofilm thickness lies within the range of 1.37 - 0.008 µm in the 5-tanks simulation configuration for the fixed bed, and up to 2 µm in the 10- tanks simulation configuration. The thickness of the microorganisms was set to 1 µm, that means that a biofilm thickness of less than 1 µm is a mean thickness representing a very dispersed biomass on the beads.

This thickness was compared to a limiting thickness of 8.8 µm at which the oxygen mass transfer limitation can not be neglected. This literature value of 8.8 µm (Cox et al., 1980) was calculated for a defined condition of dissolved oxygen concentration (45% of saturation) and a mean respiratory rate of the micro-organisms.

In the previous model, a no biofilm mass transfer limitation was then assumed, and the problem of biofilm diffusion modelling was not considered.

In order to take into account the biofilm limitation when this problem would occur (i.e. for greater biofilm thickness), the calculation of the limiting thickness for oxygen diffusion inside the biofilm and the numerical treatment of a biofilm mass transfer model were added to the previous model.

1.2.1 - Calculation of the limiting biofilm thickness for oxygen transfer

A relation, using oxygen concentration in the bulk phase and the respiratory rate of *Nitrosomonas* and *Nitrobacter*, at every moment and in every part of the column is used. This relation is based upon the equation of mass transfer rate in the biofilm for oxygen, assuming a plane geometry and no transfer resistance between the biofilm and the bulk phase (TN 27.1):

$$\frac{d^2 C_{O2}\big|_B}{db} = -\frac{1}{D_{O2}\big|_B}\left[r_{O2}^{Ns}\big|_B + r_{O2}^{Nb}\big|_B\right]$$

Assuming steady values throughout the biofilm for $D_{O2}\big|_B$, $r_{O2}^{Ns}\big|_B$ and $r_{O2}^{Nb}\big|_B$, and considering the boundary condition at the bulk phase which states that $C_{O2}\big|_B = C_{O2}\big|_L$, the theoretical biofilm thickness (h_{O2}^0) at which the oxygen concentration inside the biofilm is zero, can be approximated by the relation:

$$h_{O2}^0 = \sqrt{\frac{-2.C_{O2}\big|_B . D_{O2}\big|_B}{\left[r_{O2}^{Ns}\big|_B + r_{O2}^{Nb}\big|_B\right]}}$$

Cox et al. (1980) defined the limiting biofilm thickness for oxygen (h_{O2}^{lim}) for glass bead (diameter 1.1 mm) as the third of the thickness for which oxygen is theoretically completely exhausted:

$$h_{O2}^{lim} = \frac{h_{O2}^0}{3}$$

Assuming a spherical shape for the Biostyr beadsand no diffusion inside the beads, the same hypothesis can be used to define the limiting biofilm thickness for oxygen. The h_{O2}^{lim} calculated for the simulation of the nitrifying column using the standard configuration (as defined in TN 27.2 and reported in appendix A), lies in the range of 9 µm to 14 µm. These values are closed to the 8.8 µm of Cox et al. (1980), and as it was previously concluded, there is no oxygen transfer limitation in the biofilm in this autotrophic nitrification.

1.2.2 - Mass transfer model in the biofilm

Because there is no oxygen diffusion limitation in the biofilm, the addition of a biofilm model to the previous autotrophic nitrifying model is unnecessary. Nevertheless, a numerical treatment of a biofilm model has been made in case of future biofilm limitation problems.

If for autotrophic growth the biomass synthesis is sufficiently low to neglect the biofilm limitation, this will no be the case for higher growth as the growth in heterotrophic (organic carbon source) conditions.

The model chosen for mass transfer in a biofilm is based on the following assumptions (TN 27.1):

1 - Steady state transfer limitation in the biofilm
2 - No transfer resistance between the biofilm and the bulk phase
3 - A plane geometry is supposed for the biofilm

The model is represented, at every time t, by the following system:

$$\left.\frac{d^2 C_{Si}|_B}{db^2}\right|_b = -\frac{1}{D_{Si}|_B}\left[r_{Si}^{Ns}|_B + r_{Si}^{Nb}|_B\right]$$

with the boundary conditions

$$\left.\frac{dC_{Si}^{\alpha}|_B}{db|_B}\right|_{b=R_0} = 0$$

$$C_{Si}^{\alpha}|_B = C_{Si}^{\alpha}|_L \qquad \text{at} \qquad b = R_0 + h_b^n$$

where R_0 is the bead radius and h_b the biofilm thickness and b denotes for the the abscissa throughout the biofilm.

The system is solved using a Runge Kutta Merson algorithm of the 4^{th} order. To be solved the model previously described is decomposed into first order and second order derivatives:

$$\begin{cases} F1 = Deriv_2 = \dfrac{dDeriv_1}{db} = -\dfrac{1}{D_{Si}|_B}\left[r_{Si}^{Ns}|_B + r_{Si}^{Nb}|_B\right] \\ F2 = Deriv_1 = \dfrac{dC_{Si}|_b}{db} \end{cases}$$

By solving F1 by the Runge Kutta Merson algorithm, values of Deriv1 are obtained, and by solving F2 (i.e. Deriv1), values of $C_{Si}|_b$ are obtained (i.e the concentration profile inside the biofilm). The initial values are defined at $b = R_0 + h_b^n$:

$$C_{Si}^{\alpha}|_B = C_{Si}^{\alpha}|_L$$

$$Deriv_1 = \frac{dC_{Si}^{\alpha}|_B}{db|_B} = 0 \qquad \text{at the first integration step}$$

Because there is no boundary value for Deriv1 at $b = R_0 + h_b^n$, this value is calculated by an iterative step until the second boundary condition of the model ($\left.\frac{dC_{Si}^{\alpha}|_B}{db|_B}\right|_{b=R_0} = 0$) is reached. A general scheme for the calculation of the biofilm profile concentration is reported in figure 1.

The biofilm concentration profile for oxygen is calculated using this model for the bulk concentrations and fixed biomass obtained after a simulation of an autotrophic nitrification of 350 hours and for a standard configuration for the column (appendix A). These bulk concentrations, fixed biomass and biofilm thickness are reported in appendix B.

In figure 2, only the biofilm concentration profile of oxygen in the first part of the bed (bottom of the fixed bed) is presented.

Figure 2a shows the oxygen concentration profile for the bulk concentrations reported in appendix B.

Figure 2b shows the oxygen concentration profile for the same bulk concentrations, but for 30 time more fixed biomass (i.e 18.6 g/l for *Nitrosomonas*, 3.6 g/l for *Nitrobacter* and a biofilm thickness of 32.7 µm). With this second profile, we can check the validity of the model when the diffusion limitation occurs. Oxygen is completely exhausted at 18.7 µm deep. The value of h^0_{O2} estimated with the previous relation is 27.8 µm. The difference with the 2 values of h^0_{O2} is the result of the steady state assumption for the respiratory rates.

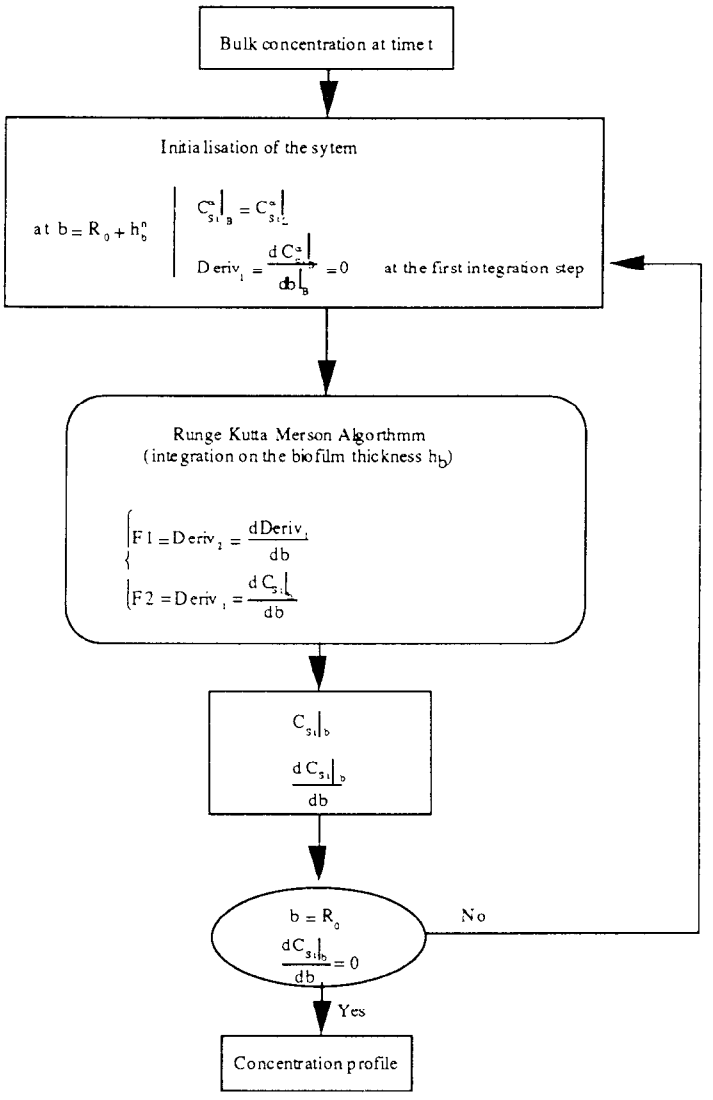


Figure 1: Algorithm for the biofilm concentration profile calculation

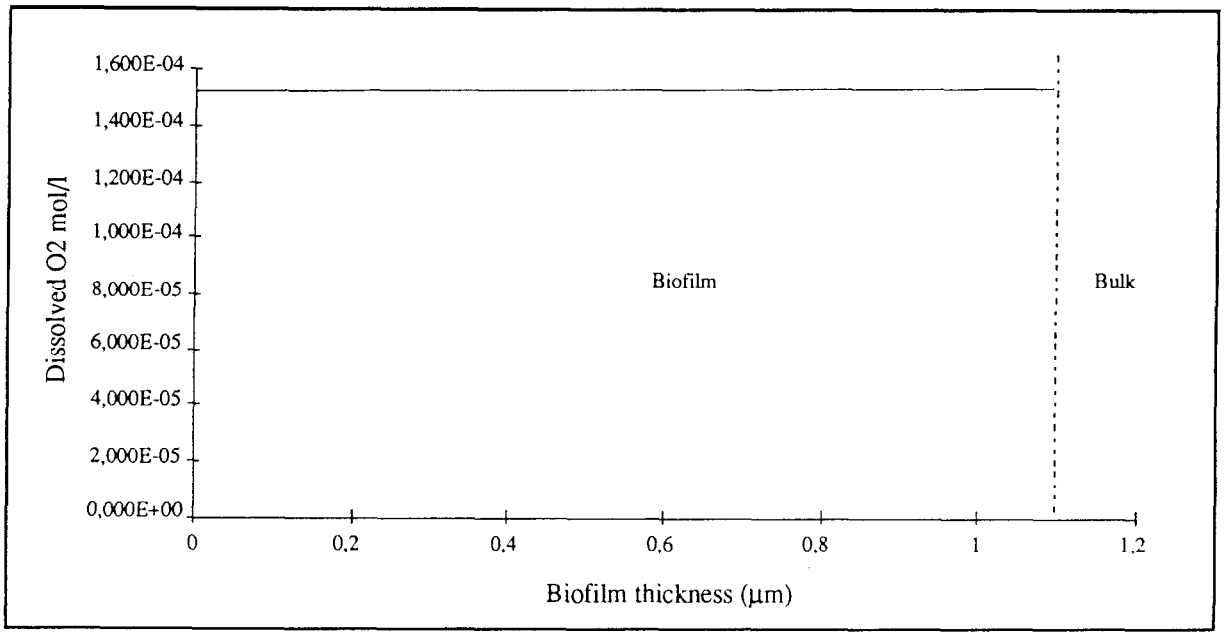


Figure 2a: Oxygen concentration profile in the biofilm of the beads in the first tank equivalent for the fixed bed.

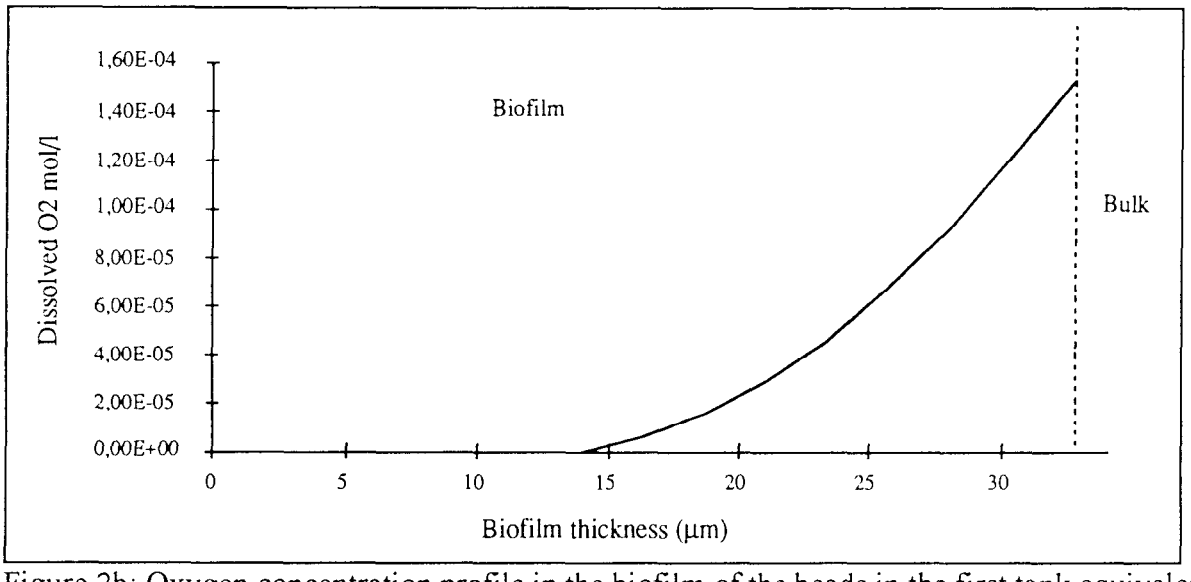


Figure 2b: Oxygen concentration profile in the biofilm of the beads in the first tank equivalent for the fixed bed with 30 times more biomass than in the conditions given in figure 2a

II - Sensitivity analysis

The sensitivity of the model for variations in the process working parameters (flow rates, numbers of tanks, back-mixing parameters) has been studied in TN 27.2. It is useful to estimate the error induced by the biological kinetic parameters because they are taken from literature (mainly from the model developed by Hunik et al., 1994). There is no evidence that the strains of *Nitrosomonas* and *Nitrobacter* used in our process have the same biological characteristics, and as shown in TN 27.1 the range of values for the maximum growth rates and cell activities is very large.

The sensitivity analysis of the model to biological parameters is studied by varying the value of these parameters in step between 0.5 and 2 times (5 times for the initial biomass) their original setting value (reported in table 1). The process working conditions (flow rates, recycling ratio, column design) used in sensitivity analysis are reported in appendix A (standard configuration of the column)

The criteria selected for the analysis of sensibility are the outlet bulk concentrations of N-compounds (HNO_2, NH_3), of oxygen, of carbon dioxide and the nitrification efficiency, defined as:

$$\frac{[HNO_3]_{out}}{[NH_3]_{input}}$$

The reference values of the parameters are reported in table 2. The sensitivity analysis is summarized in the table 3, where parameters that have an effect greater than +/- 5% on the criteria are presented as plus (+).

Table 1: Parameters analysed and their reference value. The parameters studied simultaneously are presented together.

Biological parameter	Reference value
Initial biomass for Ns and Nb	0.02 g/l
Maximal growth rate: μ_{max}^{Ns} and μ_{max}^{Nb}	0.057 h^{-1} and 0.036 h^{-1}
Maintenance coefficients: m^{Ns} and m^{Nb}	0.00338 and 0.00792 N-oxydized g biomass^{-1} oxyd. h^{-1}
Saturation constants of oxygen : K_{O2}^{Ns} and K_{O2}^{Nb}	5.05 10^{-6} mol/l and 1.7 10^{-5} mol/l
Saturation constant of NH3 K_{NH3}^{Ns} and NO2 K_{NO2-}^{Nn}	6.625 10^{-5} mol/l and 3.6 10^{-4} mol/l

Table 2: Values of the criteria in standart simulations (paretemers at their reference values).

Criteria	for a 70 hours process	for a 350 hours process
Outlet NH_3	3.20 10^{-4} mol/l	2.38 10^{-4} mol/l
Outlet HNO_2	1.97 10^{-4} mol/l	6.61 10^{-5} mol/l
Outlet dissolved O_2	2.33 10^{-4} mol/l	2.32 10^{-4} mol/l
Outlet total CO_2	8.25 10^{-4} mol/l	1.35 10^{-3} mol/l
nitrification efficiency	90.5%	95.7%

The time values of 70 hours and 350 hours were chosen in accordance with the results of the previous simulations (TN 27.2):

- 70 hours of processing (among 2.5 times the mean liquid residence time) is the end of the transient period for the simulation of nitrifying process with a standard configuration.

- after 350 hours of processing, the steady-state for the defined processing conditions is reached.

2.1 - Sensitivity to the initial biomass [figures 3a-b-c]

The sensitivity of the model to the biomass boundary conditions has been already studied in TN 27.2. This analysis is a complement for the previous study.

Figures 3a and 3b confirm the great influence of fixed biomass at t=0 in short dynamics (i.e. transient behaviours) for a defined NH_3 load (0.11 kg/m3.day). If the biomass concentration is not sufficient, the nitrite and ammonia concentrations greatly increase, and as a consequence, the nitrifying efficiency of the column is reduced. By increasing the fixed biomass at the start up of the process, nitrite and ammonia concentrations are reduced, the concentration of the dissolved CO_2 increases (indicating a lower growth rate) and O_2 and the nitrification efficiency are very little influenced.

All the effects of the biomass boundary conditions are erased with the time. At 350 hours any of the criteria have changed of more than +/- 5% (figure 3c). The biomass concentration at the start up of the process has no influence on the steady state of the process.

2.2 - Maximum growth rate [figures 4a-b-c]

The maximum growth rate of *Nitrosomonas* (μ_{max}^{Ns}) an *Nitrobacter* (μ_{max}^{Nb}) have been varied simultaneously in the range of 0.5-2 times the reference value. As for initial biomass, for lower values of μ_{max}, the N-compounds concentrations and the nitrification efficiency are greatly changed in short dynamics (figure 4a -b). As for biomass, this is a consequence of an increase of the transient period (>70 hours).

After 350 hours of processing, dissolved gas concentrations and nitrifying efficiency are not affected more than +/- 5%. But nitrite and ammonia in the outlet flow are from 0.4 to 3 times of the original concentration. Nevertheless, these variations have little influence on the nitrifying efficiency, because of the low value of these concentrations (table 2).

2.3 - Maintenance coefficient [figures 5a-b]

The maintenance coefficient of *Nitrosomonas* and *Nitrobacter* have been varied simultaneously in the range of 0.5-2 times the original value. After 70 hours of processing, N compounds concentrations and dissolved CO_2 forms are the criteria the most affected by changes in maintenance values. It can be noted that variations of N-compounds are opposite for maintenance and maximum growth rate. Oxygen and nitrifying efficiency are a few affected.

At the contrary of maximum growth rate, the ammonia and nitrite concentrations are more affected after a process of 350 hours than after 70 hours. Nevertheless, these variations have few influence on the nitrifying efficiency, because of the low value of the concentrations (table 2).

2.4 - Half saturation constant of oxygen [figures 6a-b]

Both after transient and steady state, the K_{O2}^{Ns} and K_{O2}^{Nb} values have little influence on the selected criteria. All, except nitrite concentration stay in a range of +/- 5% the original values (tables 2 and 3).

2. 5 -Half saturation constants of NH_3 (*Nitrosomonas*) and NO_2^- (*Nitrobacter*) [figures 7a-b]

The sensibility curve for the half saturation constant of N-substrates are quite similar to those for the half saturation constants of oxygen. The most affected criteria are nitrite and ammonia concentrations, which are directly linked to the studied parameters.

Conclusions of the biological parameters sensitivity analysis

As can be seen in table 3, the effects of the variations in the biological parameters values are erased with the time. At 350 hours the dissolved oxygen, the carbon dioxide concentrations, and quite less generally the nitrification efficiency, have not changed of more than +/- 5% .

For short growth periods and transient periods, these effect are more important.

After 350 hours of processing, there is no more growth, while for transient periods a biomass growth occurs. Then the biological parameters mainly affect the growth of the micro organisms. The carbon dioxide is a good indicator of the growth. When the CO_2 criterium value is greater than 1, that means that the growth is lower than in the process with standard configuration. And at the contrary, when the CO_2 criterium value is lower than 1, that means that the growth is enhanced.

In all cases, the most affected criteria are the outlet nitrite and ammonia concentrations values. Nevertheless, these sensitivities must be compared with the low values of these concentrations (table 2).

The nitrification efficiency of the process in steady state (assumed after 350 hours of processing) is little increased when the maximum growth rate of the micro-organisms is increased from the reference value (102% when μ_m is doubled), and is slighly reduced when the maintenance coefficient is increased (93% when m is doubled). As in steady state conditions for the fixed biomass the oxydation of ammonia and nitrite is mainly due to maintenance, these results can be explained by the growth model:

In steady state conditions for the fixed biomass, and assuming no biomass release in the liquid, it can be written:

$$R_X = 0$$

The specific growth rate in steady state conditions is then imposed by m, the maintenance coefficient and μ_m, the maximun growth rate:

$$\mu^{PSP} = \frac{Y_{X/Smt.m}}{\left[1 + \frac{Y_{X/Smt.m}}{\mu_m}\right]}$$

As previoulsy defined, μ is a function of substrates concentrations:

$$\mu = \mu_{max} \prod_k \frac{C_k}{(Ks_k + C_k)} \frac{1}{K_{I-k}}$$

Then in steady state, the concentrations are controlled by m and μ_m.

If μ increases, then substrate concentrations (NH_3, NO_2^-) will incease, and as a consequence, the nitrification efficiency defined as $\frac{[HNO_3]_{out}}{[NH_3]_{input}}$ is reduced.

The relation $\mu^{PSP}=f(\mu_m,m)$ indicates that μ^{PSP} is more greatly affected by m than by μ_m. If the maintenance coefficient increases, then μ^{PSP} increases and the nitrification efficiency decreases. If μ_m increased, μ^{PSP} stay quite unchanged. Then considering the definition of μ, if μ^{PSP} is unchanged and μm is increased, then the substrates concentrations (NH_3, NO_2^-) are reduced and the nitrification is increased.

The efficiency is reduced when the half saturation constants are increased. As for m and μ_m, these result can be explained by the expression of μ^{PSP}.

Table 3: Results of the sensitivity of the model to biological parameters.
(-: less than 5%; + between 5% and 7%; ++ between 7% and 10 %; +++ greater than 10%)

	70 hours process					350 hours process				
	NH_3	HNO_2	O_2	CO_2	Nit. eff.	NH_3	HNO_2	O_2	CO_2	Nit. eff.
Initial biomass for Ns and Nb	+++	+++	-	+++	+++	-	-	-	-	-
Maximal growth rate: μ_{max}^{Ns} and μ_{max}^{Nb}	+++	+++	-	+++	+++	+++	+++	-	-	-
Maintenance coefficients: m^{Ns} and m^{Nb}	+++	+++	-	+++	-	+++	+++	-	++	+
Saturation constants of oxygen : K_{O2}^{Ns} and K_{O2}^{Nb}	+	+++	-	-	-	-	++	-	-	-
Saturation constant of NH3 K_{NH3}^{Ns} and NO2 K_{NO2-}^{Nb}	+++	+++	-	-	+++	+++	+++	-	-	+

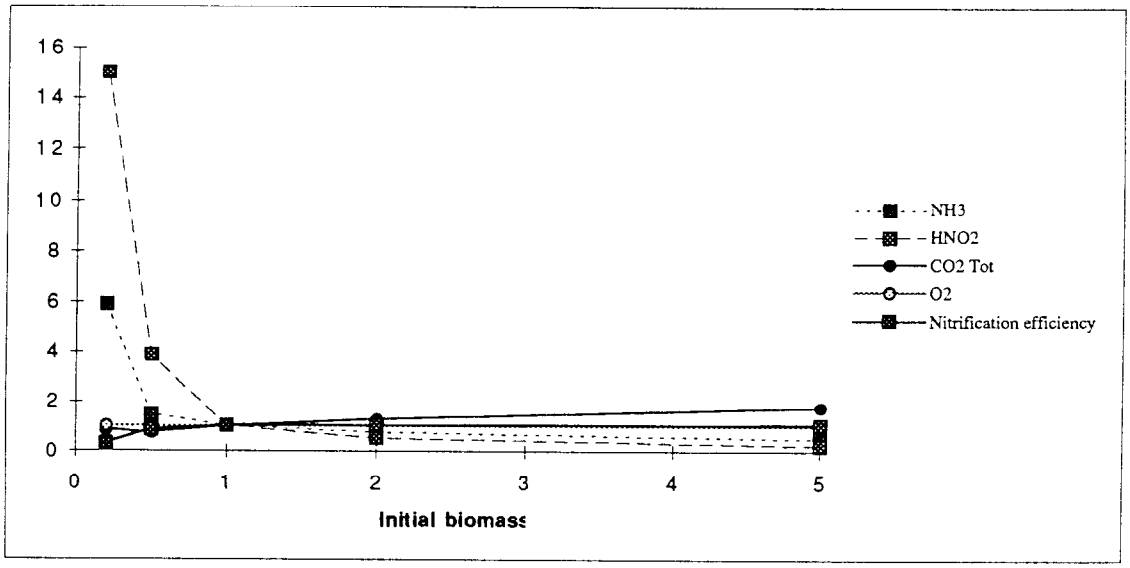


Figure 3a: Sensitivity analysis at 70 hours for initial biomass

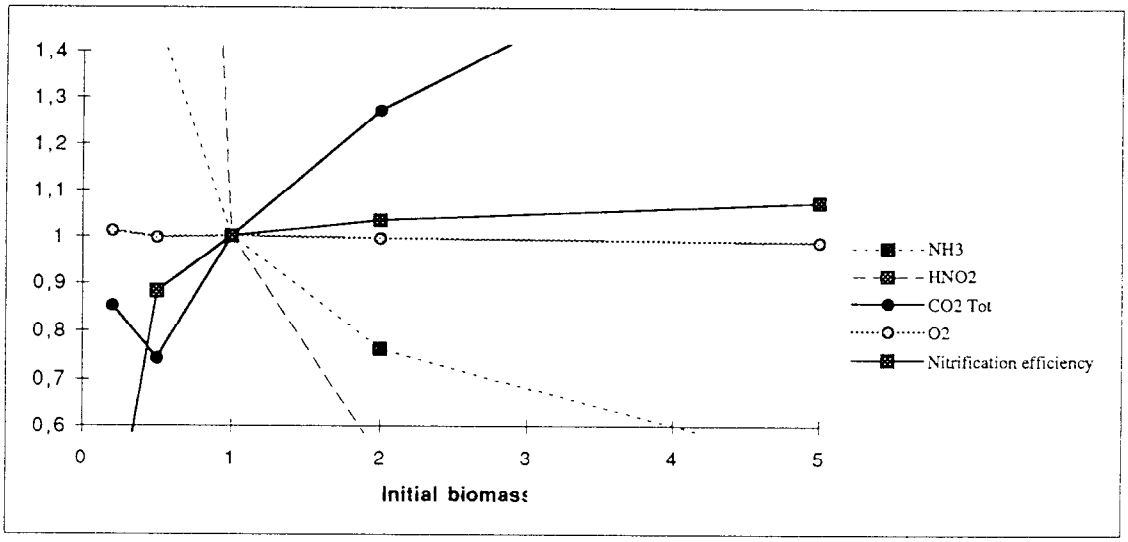


Figure 3b: Sensitivity analysis at 70 hours for initial biomass (enlarged scale of figure 3a)

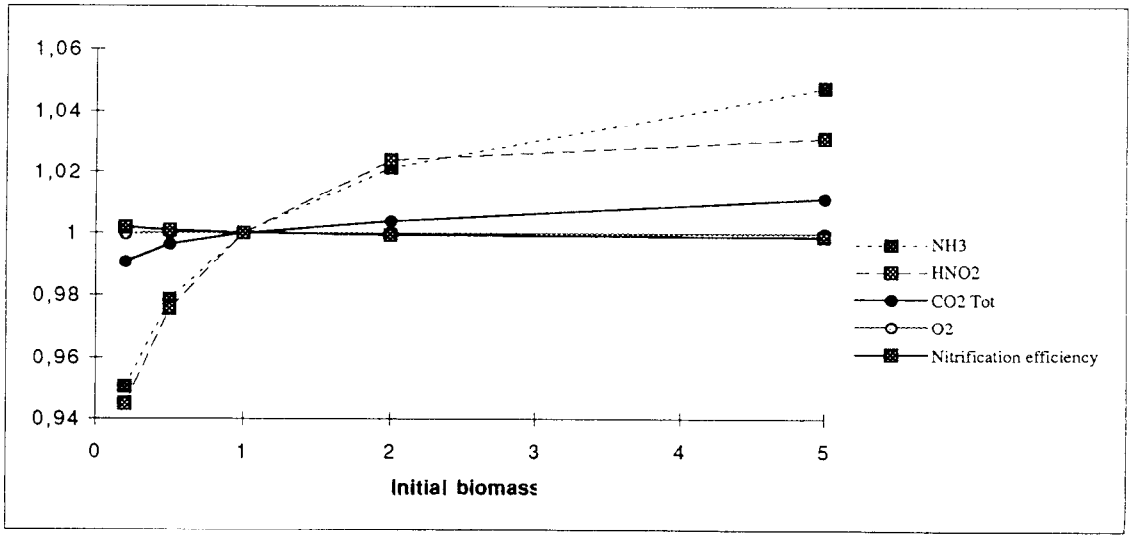


Figure 3c: Sensitivity analysis at 350 hours for initial biomass

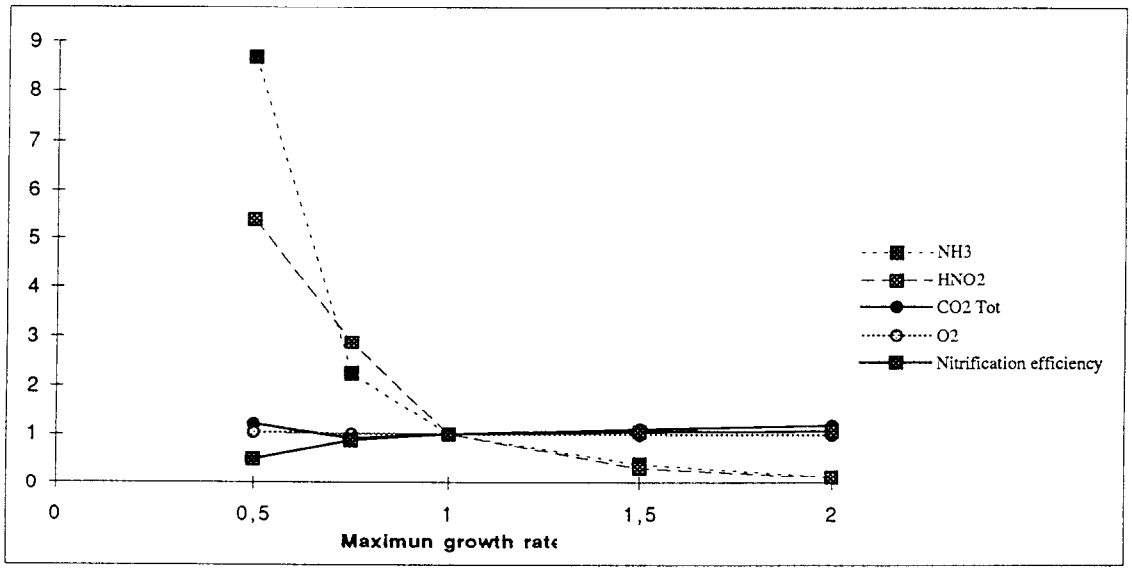


Figure 4a: Sensitivity analysis at 70 hours for maximun growth rates

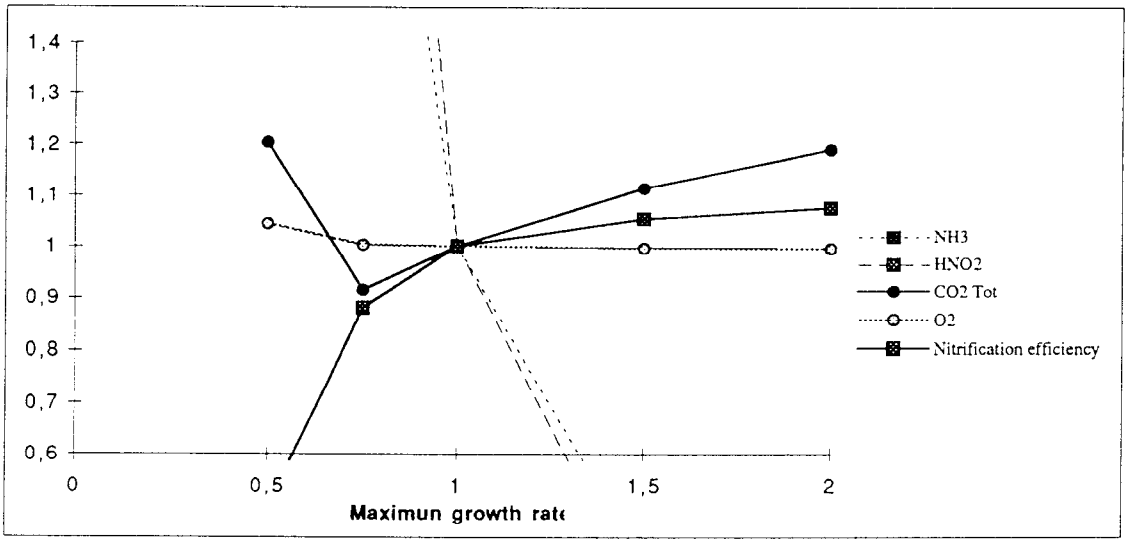


Figure 4b: Sensitivity analysis at 70 hours for maximun growth rates (enlarged scale of figure 4a)

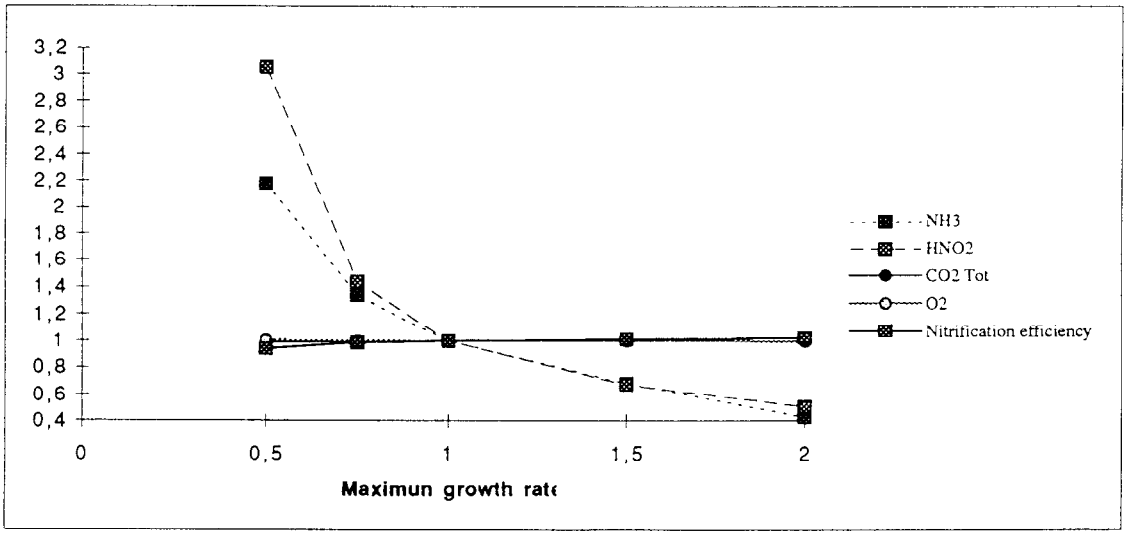


Figure 4c: Sensitivity analysis at 350 hours for maximun growth rates

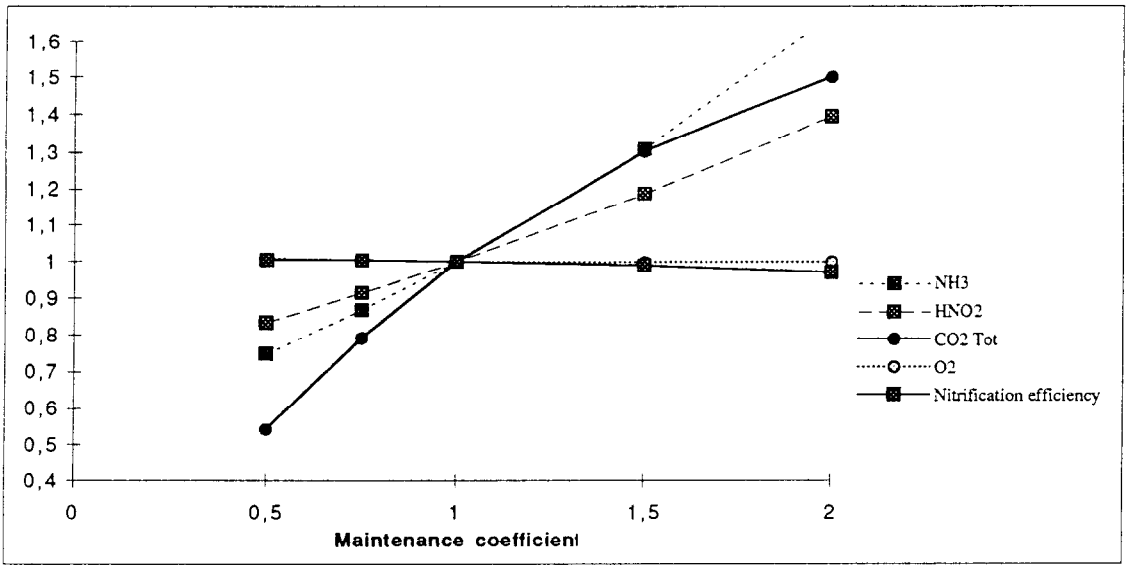


Figure 5a: Sensitivity analysis at 70 hours for maintenance coefficient

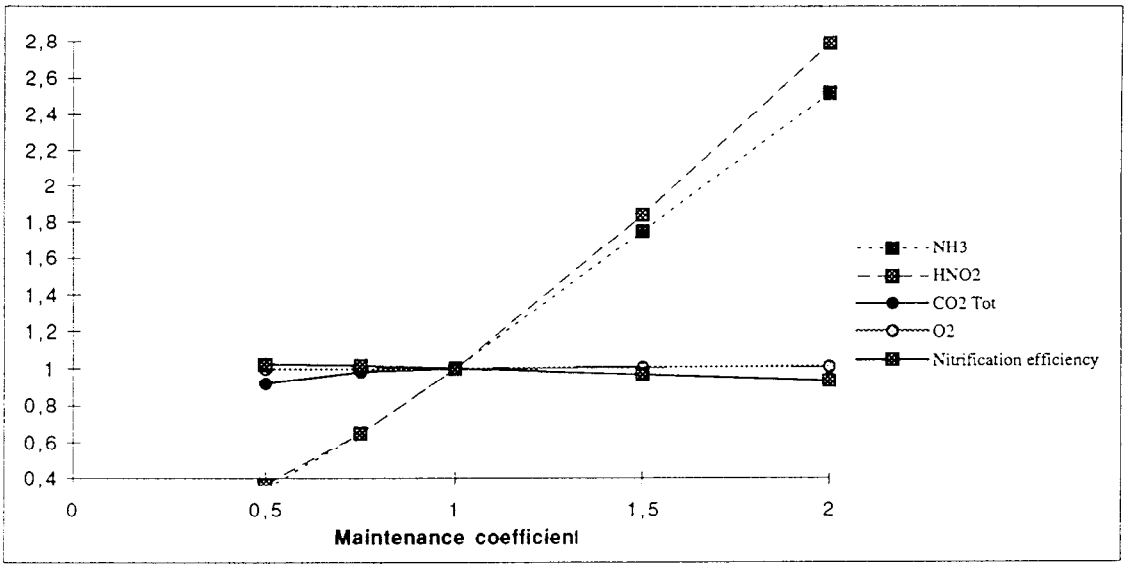


Figure 5b: Sensitivity analysis at 350 hours for maintenance coefficient

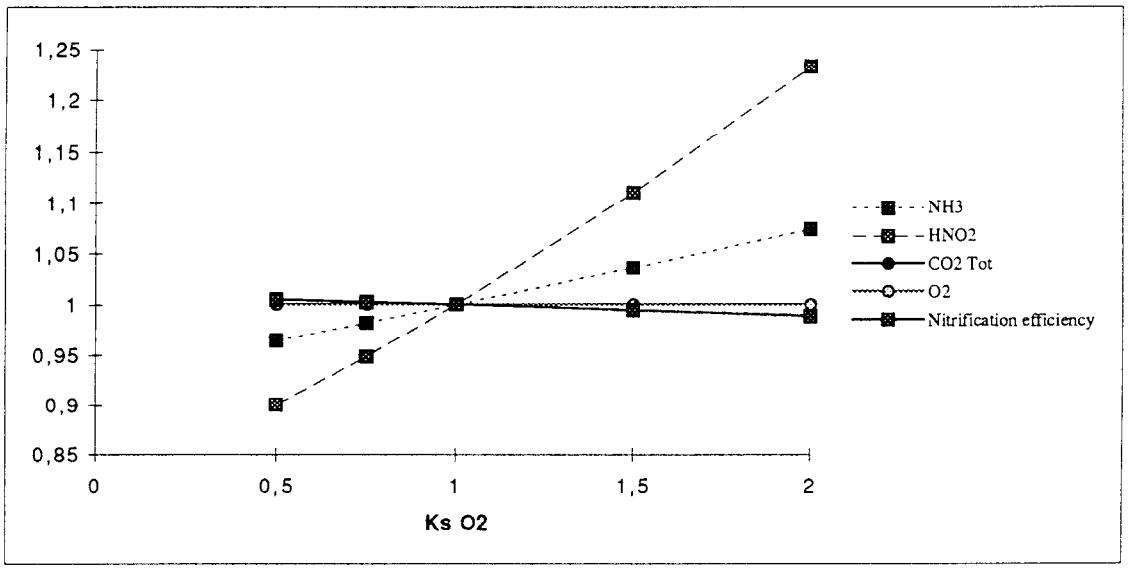


Figure 6a: Sensitivity analysis at 70 hours for saturation constant of oxygen

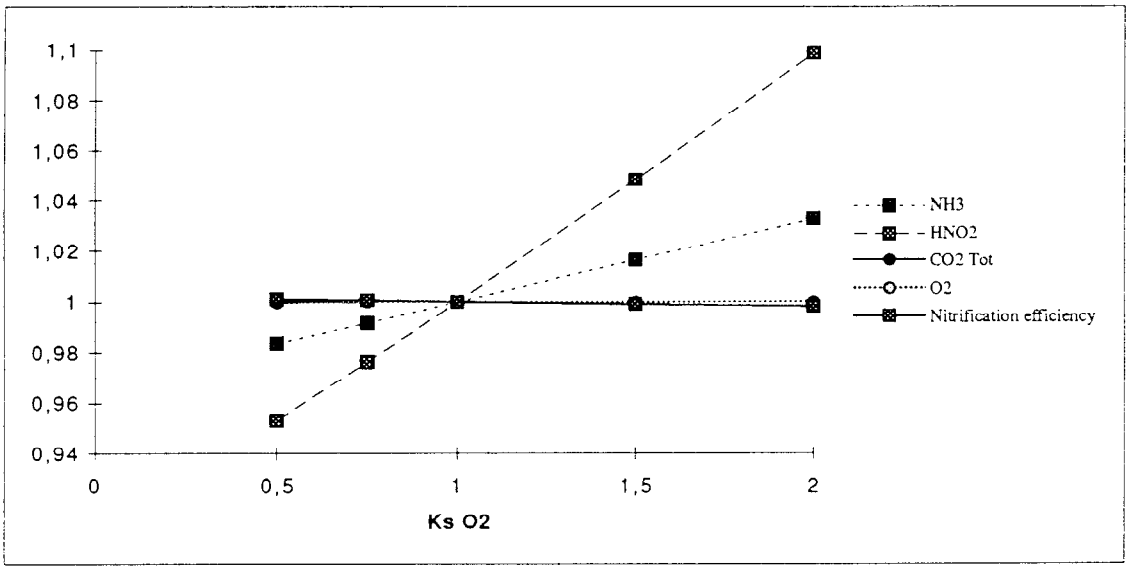


Figure 6b: Sensitivity analysis at 350 hours for saturation constant of oxygen

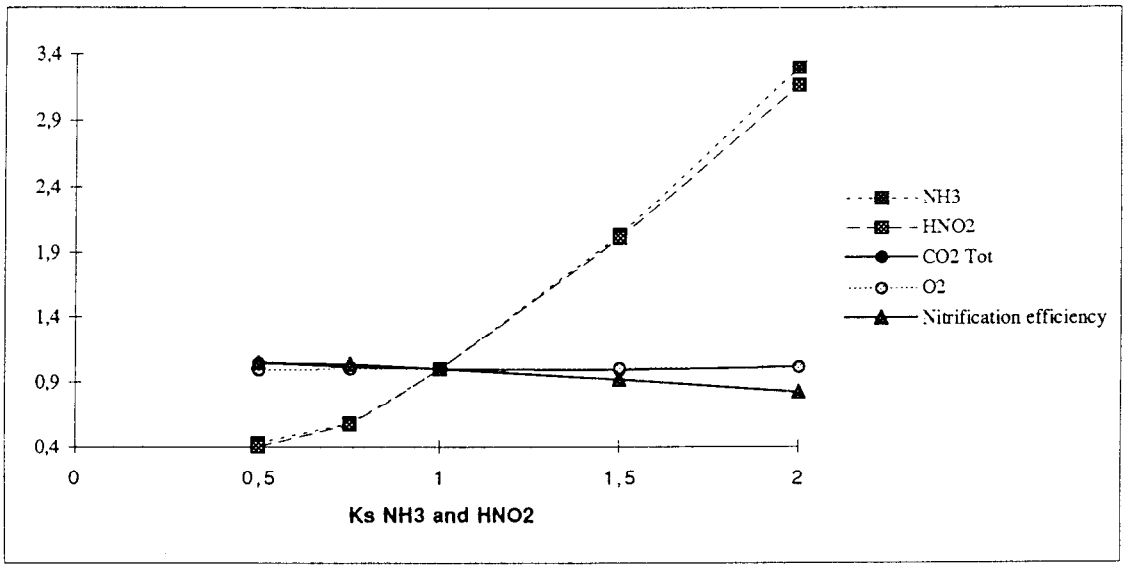


Figure 7a: Sensitivity analysis at 70 hours for saturation constant of NH3 and NO2-

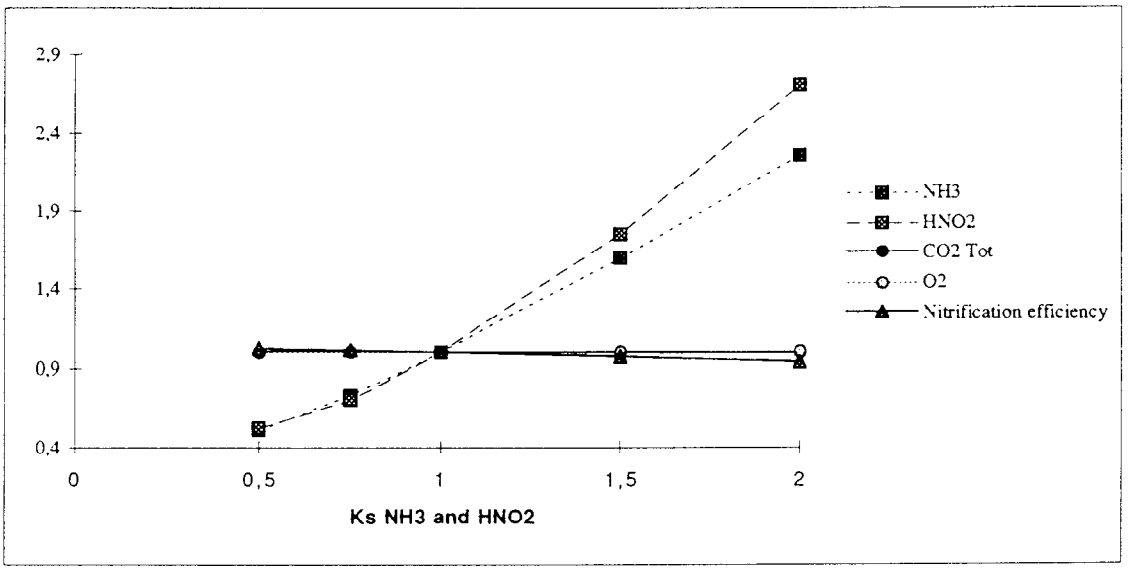


Figure 7b: Sensitivity analysis at 350 hours for saturation constant of NH3 and NO2-

III - Short dynamics and transient behaviour

The residence time (RTD) analysis presented in TN 27.2 have shown that for short dynamics, the back-mixing parameters f (for liquid) and f' (for gas) are of great importance for the flows behaviour. For the description of the fixed bed column, 3 flow parameters must be identified:

N: the number of tanks in series describing the fixed bed
f: the liquid back-mixing inside the bed
f': the gas back-mixing inside the bed

The Liquid RTD experiments held in the UAB laboratory conclude that the fixed bed is a 1 tank equivalent (TN 25.330). It is rigth that for the liquid phase, the fixed bed has the behaviour of a 1-tank model. Nevertheless, this conclusion can not be extends to the biomass because the bacteria are fixed on beads and are not mixed in the liquid flow. The simulations (TN 27.2) have shown that a 5 or 10 tanks representation of the bed allows a variable distribution of the micro-organisms (*Nitrosomonas* and *Nitrobacter*) inside the bed, giving results in accordance with literature observations on the biomass distribution in nitrifying columns (Cox et al. 1982).

Thus RTD analysis begun in TN 27.2 was continued to identifyed the different flow parameters.

3.1 - RTD analysis

3.1.1 - Liquid flow parameters, N and f, identification

From experimental data obtained at UAB laboratory (Appendix C), the identification of the model parameters N and f can be made. The identification of the model parameters is realised using a Gauss-Newton method by minimizing the criteria $\sum\left[(\text{exp. value} - \text{model value})^2\right]$.

In figures 8a-b and 9a-b, the RTD curves identified from respectively experiment 2 and experiment 3 (appendix 3), are reported and compared to these experimental data. The RTD data were obtained by UAB laboratory for the fixed bed column fed with liquid at 2.8 ml/min and a recycling flow rate of 45 ml/min with a pulse tracer input (blue dextran) of 1 g. With close criteria values, the liquid back-mixing parameters identified are very different between the 2 experiments (table 4). This indicates the great sensibility of this parameter.

Figures 8c-d and 9c-d, present the relative deviation of the model values to the experimental ones.

It appeared that the simultaneous identification of the 2 parameters N and f was impossible. As reported in figure 10, and as it can be seen in table 4, for a fixed value of the number of tanks in series for the fixed bed, the value of the liquid back mixing (f) increases linearly. The back mixing compensates the plug flow behaviour introduced by increasing the number of tanks, in order to obtain the perfectly mixed behaviour for the liquid phase. That is the reason why all the simulated RTD curves (figure8a-b and 9a-b) are identical for different numbers of tanks.

The 2 flow parameters N and f are thus difficult to dissociate. It was suggested that for RTD analysis of the fixed bed column with no recirculation, the influence of f would be sufficiently low to determine the number of tanks in series. Simulations of RTD without recirculation (figures 11a-b) show that with a liquid back-mixing of 155% of the total liquid flow rate inside the bed (obtained from the identification with experiment 3 and for a 5 tanks in series representation for the fixed bed), the determination of N stays hazardous.

Nevertheless, it must be emphasized that the value of 155% has been identified for a total liquid flow rate inside the bed of 47.8 ml/min. In RTD simulation reported in figure 11a, the

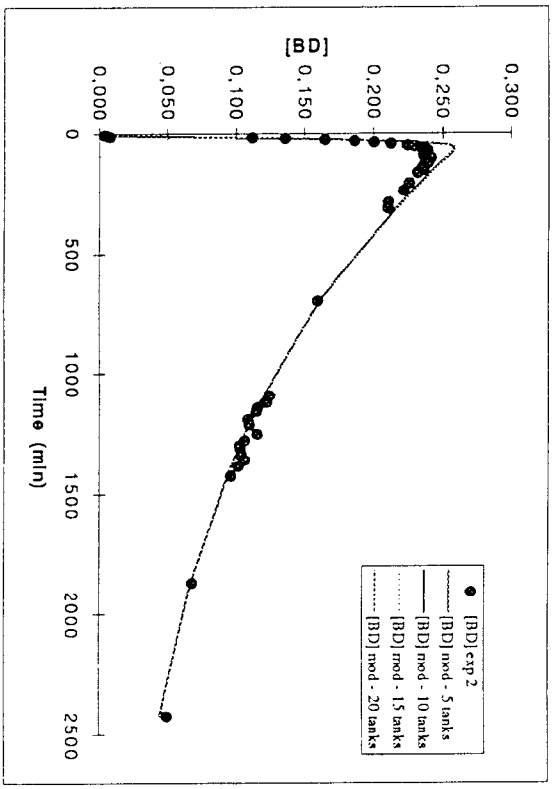


Figure 8a Data points of experiment 2 (Blue Dextran) and model curves identified from these points for different N-tanks configuration

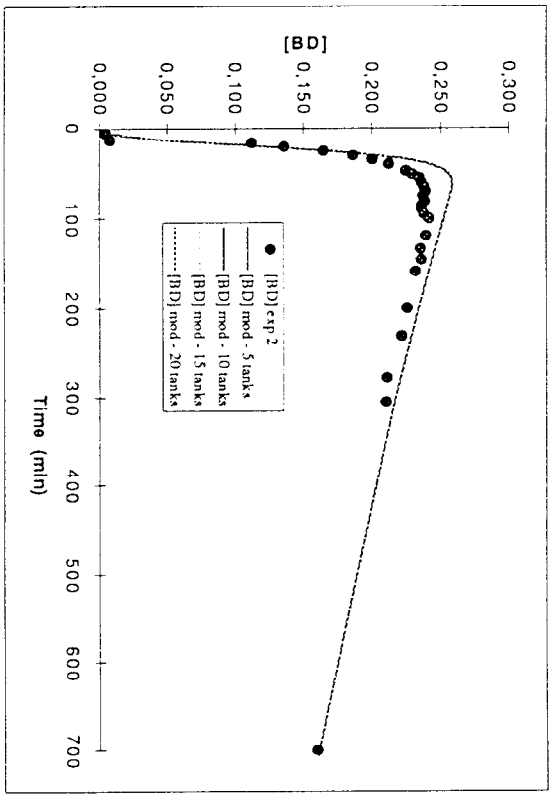


Figure 8b Data points of experiment 2 (Blue Dextran) and model curves identified from these points for different N-tanks configuration

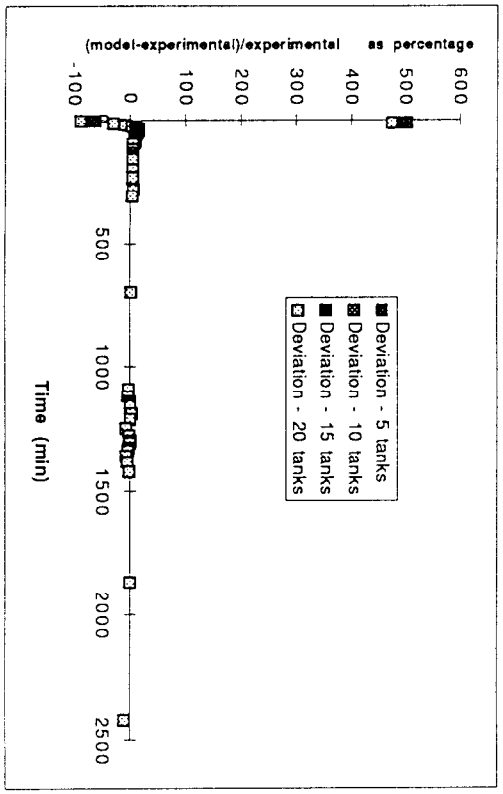


Figure 8c Relative deviation of model curves from Data points of experiment 2 (model-exp)/exp

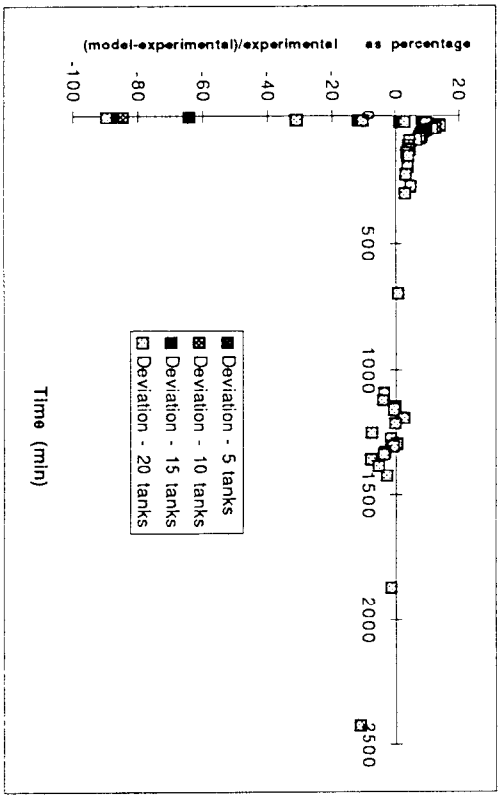


Figure 8d Relative deviation of model curves from Data points of experiment 2 (model-exp)/exp

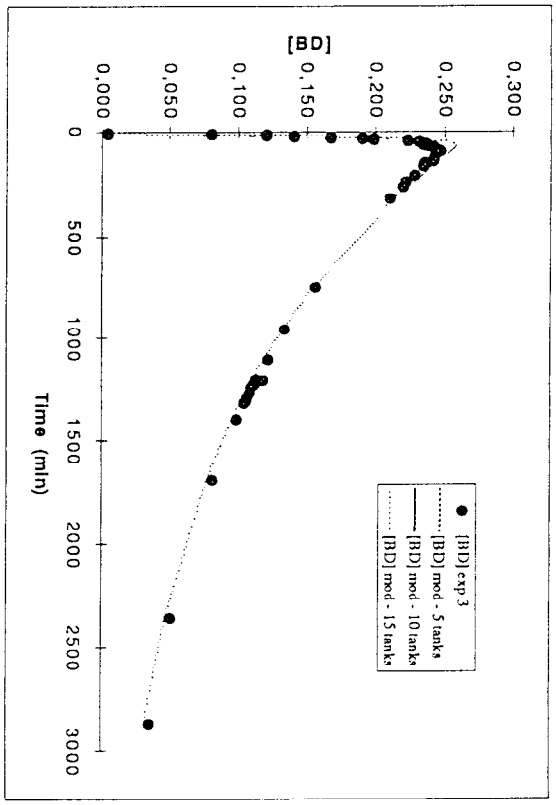


Figure 9a Data points of experiment 3 (Blue Dextran) and model curves identified from these points for different N-tanks configuration

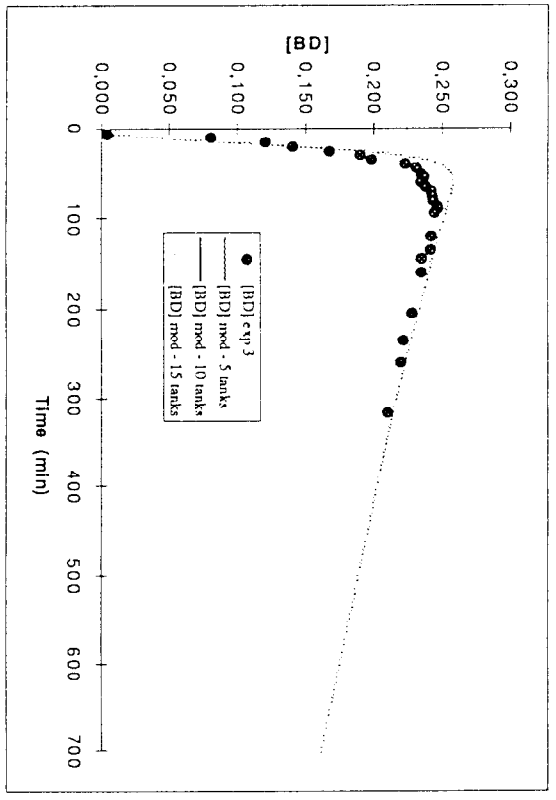


Figure 9b Data points of experiment 3 (Blue Dextran) and model curves identified from these points for different N-tanks configuration

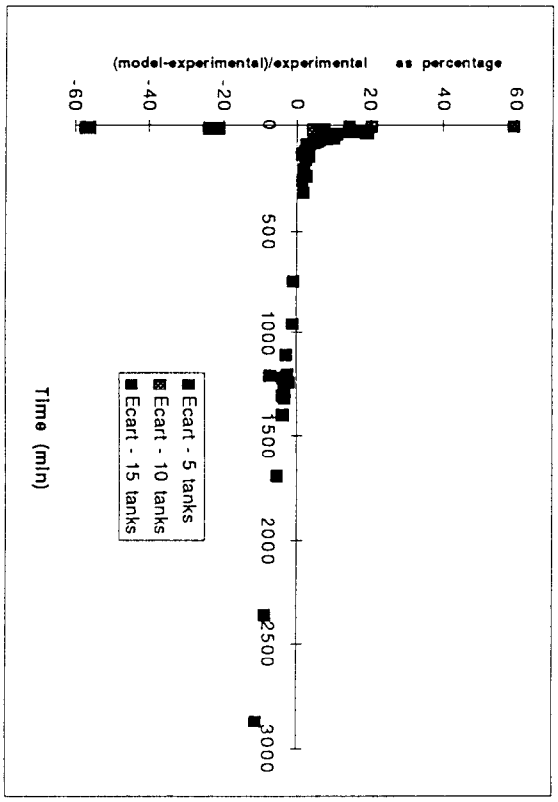


Figure 9c Relative deviation of model curves from Data points of experiment 3 (model-exp)/exp

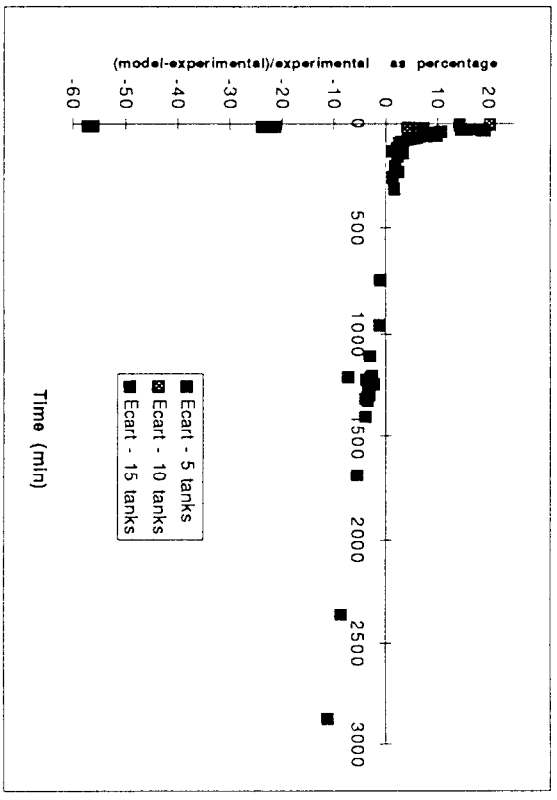


Figure 9d Relative deviation of model curves from Data points of experiment 3 (model-exp)/exp

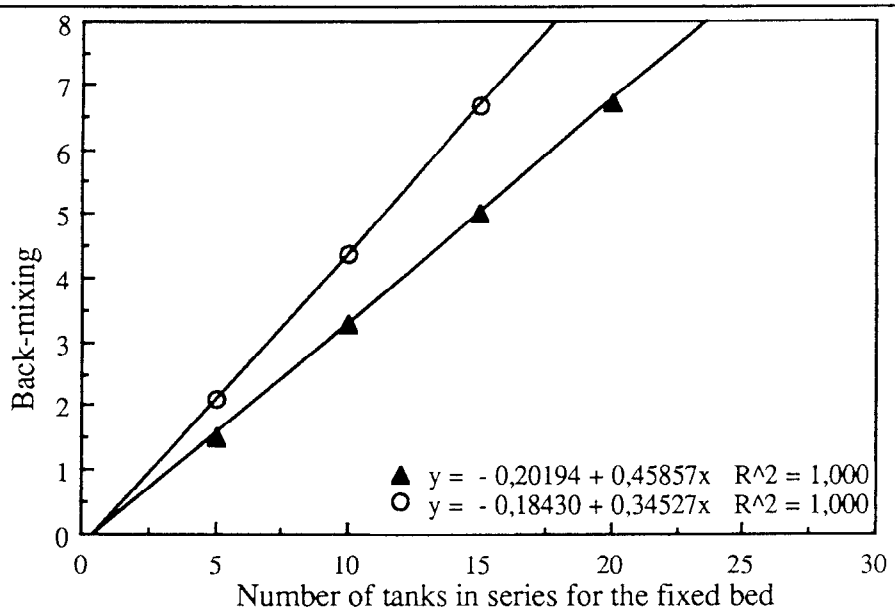


Figure 10: The liquid bak-mixing identified from experiments 2 and 3 as function of tanks configuration

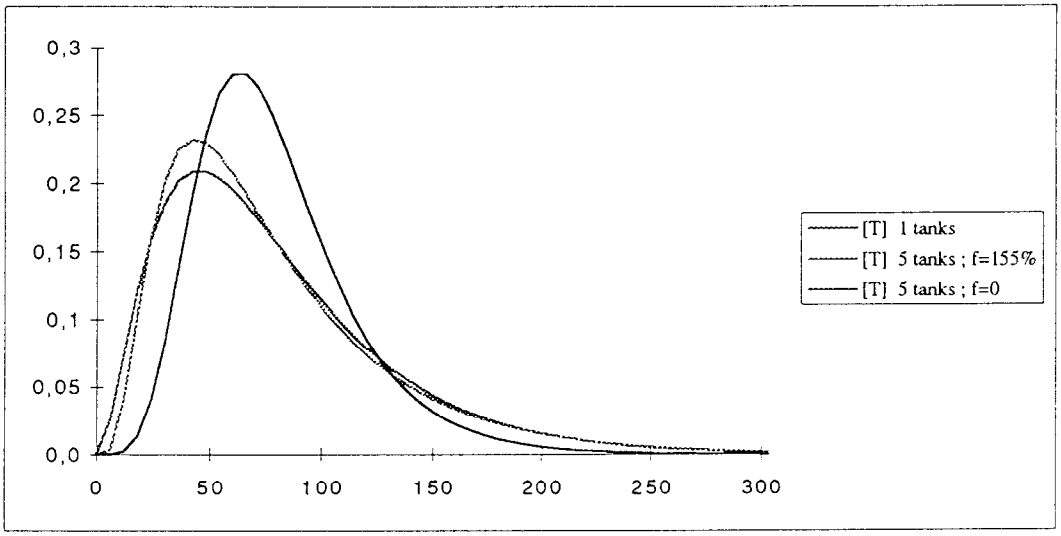


Figure 11a: Liquid RTD curves simulated with no recycling and an input flow rate of 47.8 ml/l

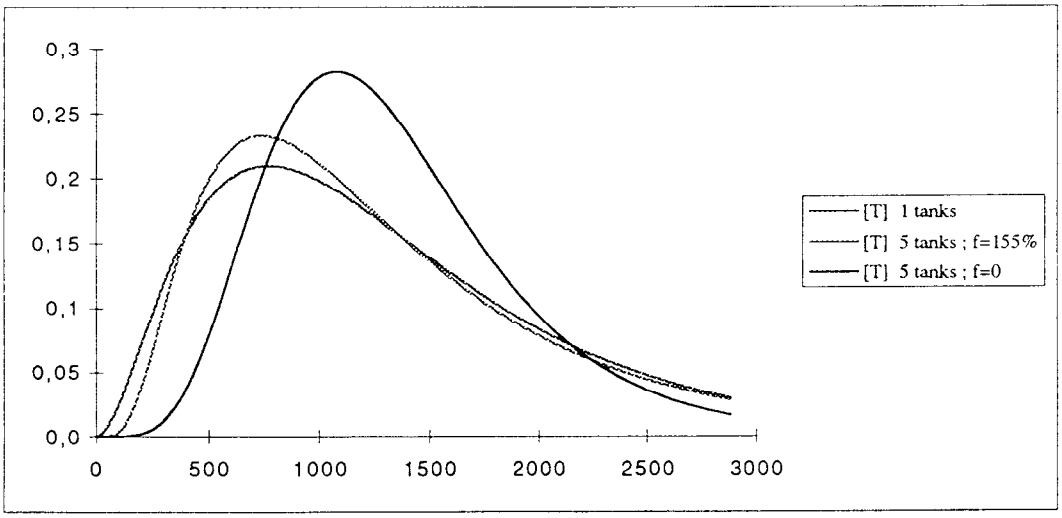


Figure 11b: Liquid RTD curves simulated with no recycling and an input flow rate of 2.8 ml/l

liquid flow rate of 47.8 ml/min is used as input flow (and no liquid recycling), but in figure 11b the input flow rate is 2.8 ml/min. If the back-mixing depends on the flow rate, it can be supposed that for the second RTD simulation (figure 11-b), the real value of f is lower than 155%. In such a case, the number of tanks in series for the bed can probably be estimated from RTD experiments with no recirculation and low input flow rate.

In conclusion, the number of tanks in series necessary for the represention of the fixed bed can not yet be determined. The assumption of 5 tanks in series is conserved, allowing a biomass distribution inside the bed and no excessive computational time. The liquid back-mixing will be set to 155% to perform the future short time simulations.

Because the biomass distribution is the main reason why the N tanks in series representation is conserved, it could be interesting to simulate this distribution for different number of tanks (that was made for 1, 5 and 10 tanks in TN 27.2), and to define a maximum and an optimal N tanks in series representation.

Table 4: Back-mixing parameters identified for different N-tanks in series representation of the fixed bed.

Number of tanks for the fixed bed	value of the back-mixing parameter	
	With data points of experiment 2	With data points of experiment 3
5	2.09	1.55
10	4.39	3.28
15	6.67	5.00
20	-	6.71

3.1.2 - Residence Time Distribution for gases

Residence Time distribution curves are simulated for different N and f' (gas back mixing parameter). The simulated curves reported in figures 12 and 13, show that the high gas input flow rate (0.03 l/min) associated with the high gas recycling ratio (99) (i.e. a total gas flow rate of 3 l/min inside the column), lead to have a perfectly mixed behaviour for the gas phase, whatever are the values of N (number of tanks equivalent for the fixed bed) and f'.

The mean residence time of the gas in the column is 12.15 minutes. Inside the column (considering the gas flow rate of 3l/min inside the column), the mean residence time is 8 seconds.

It can be reasonably assumed that the parameters N and f' play a role in our process for times constants sufficiently short to be neglected. As a consequence it does not appears to be necessary to determine a value for the gas back mixing parameter, which can be set to 0%.

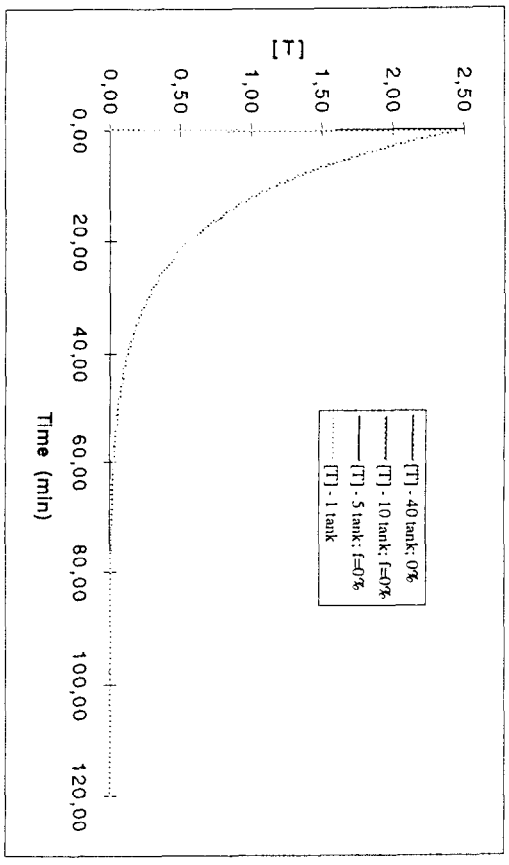


Figure 12a: Gas RTD curves for different tank configuration

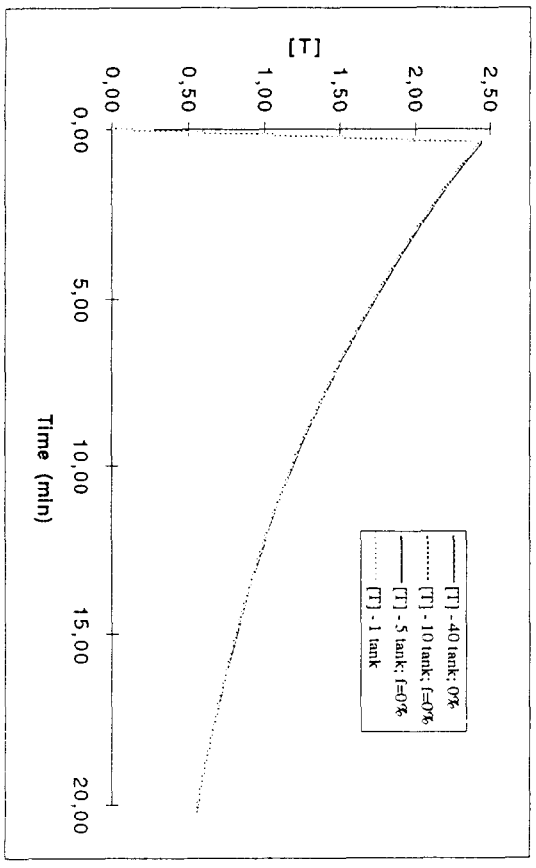


Figure 12b: Gas RTD curves for different tank configuration

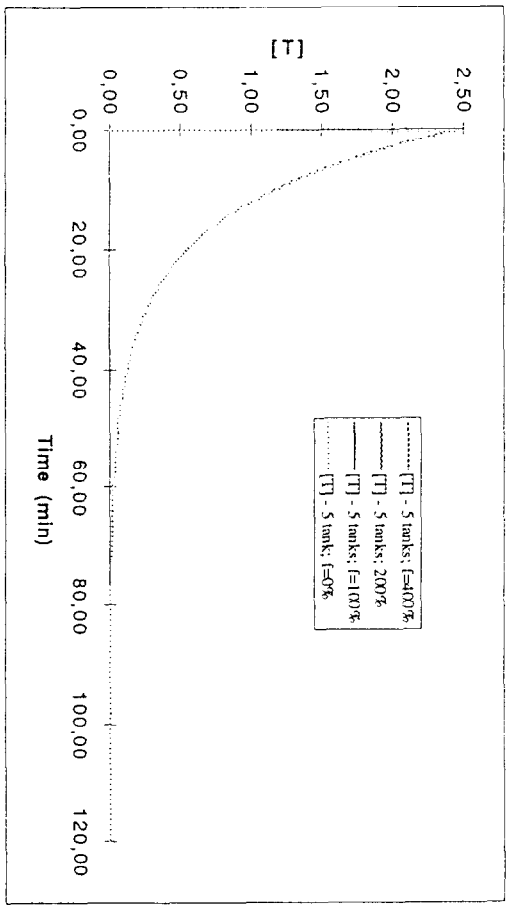


Figure 13a: Gas RTD curves for different values of gas bak-mixing and a 5 tanks configuration

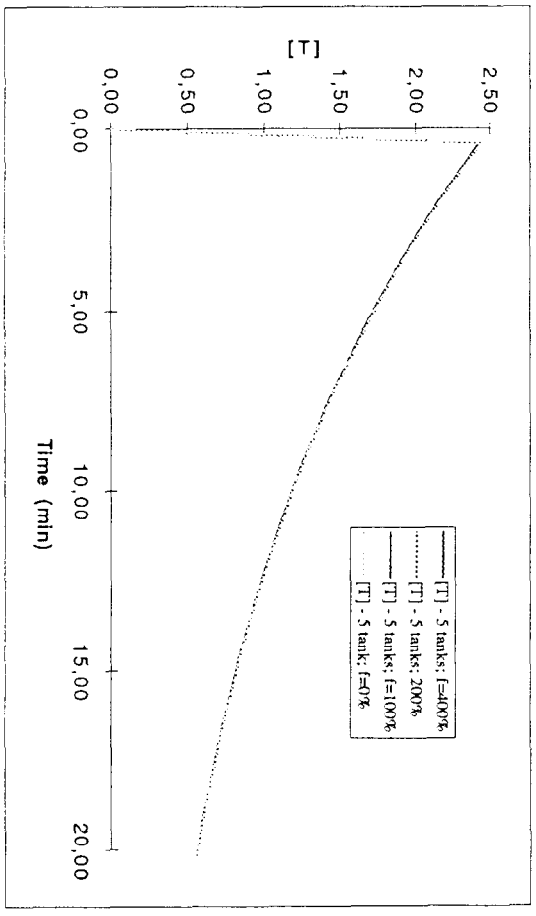


Figure 13b: Gas RTD curves for different values of gas bak-mixing and a 5 tanks configuration

3.2 - Simulation of transient behaviours

Transient behaviours are simulated with the model developed for the nitrifying fixed bed column. The flow parameters values of N, f and f' are, in these simulations, respectively set to 5, 155% and 0%. The simulations are performed from the column conditions obtained after a nitrifying process of 350 hours for a standard configuration (appendix A and B)

3.2.1 - Oxygen shutdown [figures 14]

A three step process is simulated:

0-4 hour: standard inputs on the column (appendix A).
4-16 hour: oxygen shutdown (0% of oxygen in the input gas flow, the 4000 ppm of CO_2 are conserved).
16-28 hour: standard inputs on the column are applied again (21% of oxygen in the input gas flow).

The results of the simulation are reported in figures 14 as bulk concentrations (NH_3, HNO_3, HNO_2, O_2, CO_2), mean biomass concentration, mean *Nitrosomonas* ratio inside the column, and the nitrifying efficiency of the process. Dashed lines separates the different steps.

The nitrite peak observed at 5 hours (1 hour after O_2 shutdown) is the result of the difference of the O_2 limiting concentration between Nitrosomonas (K_{O2}=5.05 10^{-6} mol/l) and Nitrobacter (K_{O2}= 1.7 10^{-5} mol/l). At 5 hour , the dissolved oxygen concentration reaches 10-5 mol/l and the nitrite oxydation becomes oxygen limited (accumulation of the nitrite produced by Nitrosomonas). At 6 hour, the dissolved oxygen concentration reach 10-6 mol/l and both ammonia and nitrite oxydation are oxygen limited.

The oxygen shutdown is quickly followed by an ammonia and a nitrite concentrations increase, and by a fixed biomass concentration decrease. The increase in the carbon dioxide can be linked to the absence of growth.

After the oxygen shutdown, all concentrations will tend to their steady state previous value excepted the mean fixed biomass concentration which stay a bit lower. A nitrite peak can be observed during the 6 hours following the oxygen return. This is the result of the more important growth of *Nitrosomonas* compared to *Nitrobacter*, as can be seen in figure 14-f.

The nitrifying efficiency falls to 55% after 12 hours of oxygen shutdown, but is 95% again 12 hours after the return of normal conditions. It can be noticed that there is a delay of approximatively 1 hour between the shutdown and its first effects. That can be related to the mean time of 1.2 hours needed for a compound in the liquid phase to go from the bottom to the top of the column.

Figure 14c Simulation of an oxygen shutdown - Evolution of the dissolved O2 concentration in liquid outlet

Figure 14a Simulation of an oxygen shutdown - Evolution of NH3 and HNO3 concentration in liquid outlet

Figure 14b Simulation of an oxygen shutdown - Evolution of HNO2 concentration in liquid outlet

Figure 14d Simulation of an oxygen shutdown - Evolution of total dissolved CO2 concentration in liquid outlet

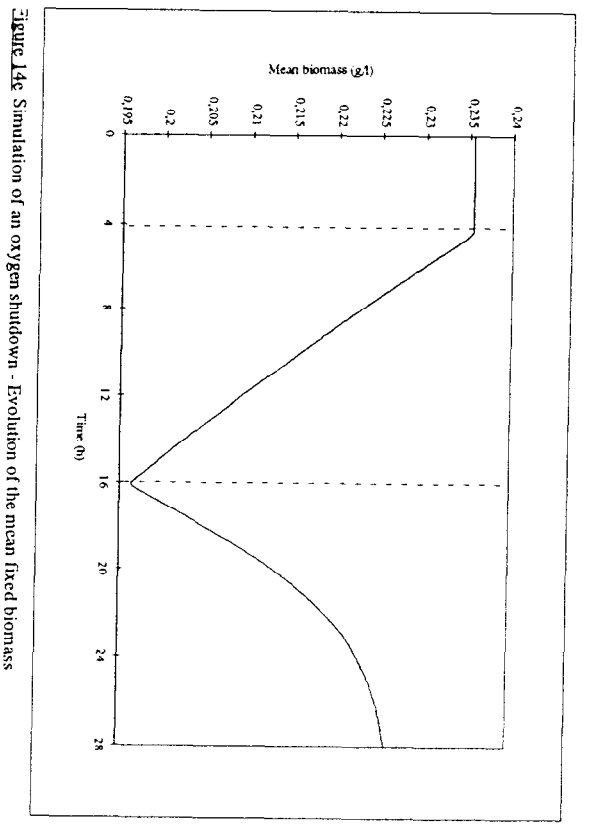


Figure 14c Simulation of an oxygen shutdown - Evolution of the mean fixed biomass

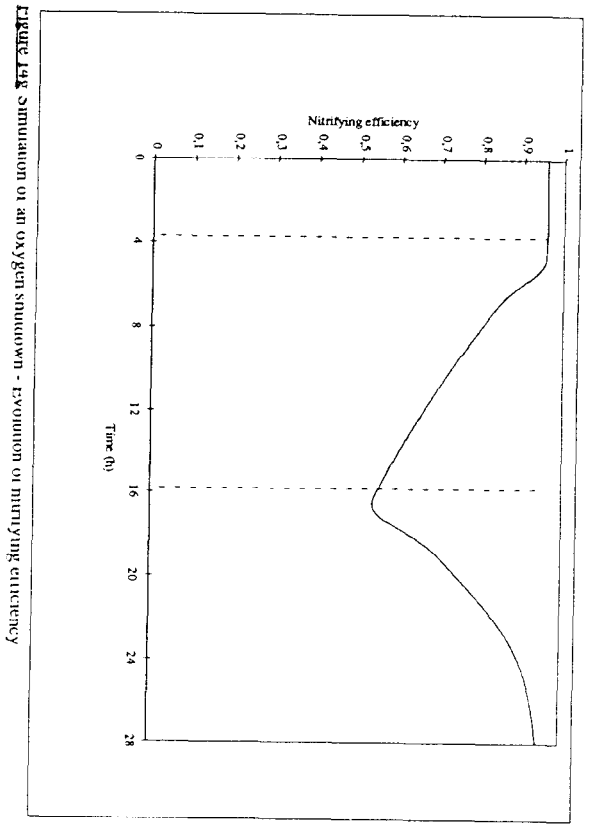


Figure 14b Simulation of an oxygen shutdown - Evolution of nitrifying efficiency

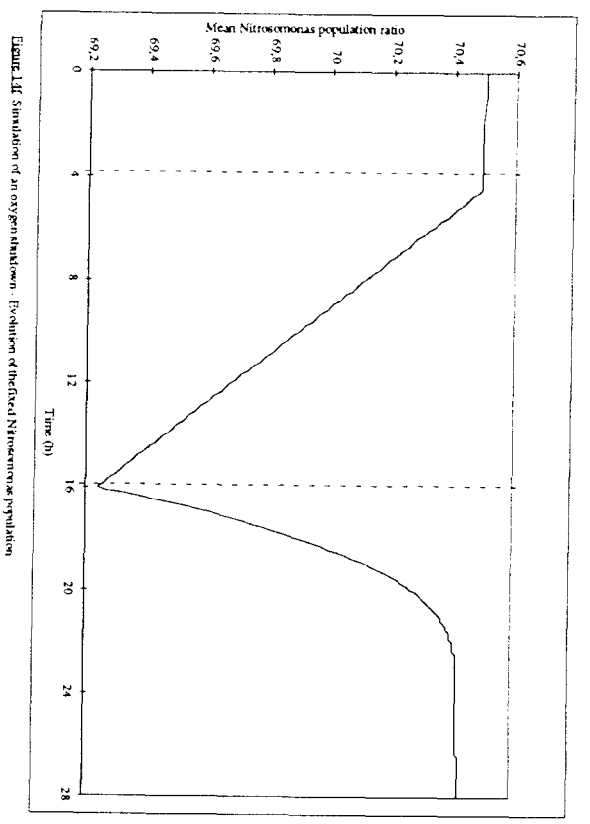


Figure 14d Simulation of an oxygen shutdown - Evolution of the fixed Nitrosomonas population

3.2.2 - Liquid flow rate variations

A five steps process is simulated:

0-4 hour: standard inputs on the column (appendix A). N-NH_3 load of 0.11 kg/m^3.day

4-16 hour: liquid input flow rate set to 7 ml/min; the recycling is maintained to 18 ml/min. N-NH_3 load of 0.28 kg/m^3.day

16-40 hour: standard inputs on the column are applied again (liquid flow rate of 2.8 ml/min). N-NH_3 load of 0.11 kg/m^3.day

40-52 hour: liquid input flow rate set to 1 ml/min; the recycling is maintained to 18 ml/min. N-NH_3 load of 0.04 kg/m^3.day

52-76 hour: standard inputs on the column are applied again (liquid flow rate of 2.8 ml/min). N-NH_3 load of 0.11 kg/m^3.day

The results of the simulation are reported in figures 15 as bulk concentrations (NH_3, HNO_3, HNO_2, O_2, CO_2), mean biomass concentration, mean *Nitrosomonas* ratio inside the column, and as the nitrifying efficiency of the process. Dashed lines separates the different steps.

By increasing the liquid input flow rate from 2.8 ml/min to 7 ml/min, the nitrifying efficiency falls to 80%. This is a consequence both of an ammonia and of a nitrite concentrations increase in the outlet stream. The nitrite peak is a consequence of the growth the *Nitrosomonas* population (both the mean fixed biomass and the *Nitrosomonas* ratio increase). The biomass growth is stimulated by the N-NH_3 load, shifting from 0.11 to 0.28 kg/m3.day.

As previously noted, the biomass growth is associated with a decrease in the dissolved carbon dioxide concentration (figure 15-d), and the carbon source at 16 hours is near to becomes limiting.

About 6 hours after the return to the standard processing conditions (input flow rate of 2.8 ml/min), the nitrate, the ammonia, the nitrite and the dissolved oxygen concentrations have reached their original values. For biomass and carbon dioxide, even after 24 hours, the original steady state situation is not reached: the biomass decrease is very slow (figure 15-e), depending only on the maintenance coefficient (see the biological kinetics, TN 27.1).

An other simulation, not presented here, was made considering the 2 first steps and maintening the third step (return to the standard working conditions) during 72 h. The mean biomass concentration of 0.252 g/l obtained at the end of these third step has not reached the original value of 0.236 g/l.

By reducing the flow rate (from 2.8 ml/min to 1 ml/min), the effect of the flow rate increase are inverted:

- ammonia and nitrite concentrations decrease
- nitrate concentration and nitrifying efficiency increase (figure 15-g)
- carbon dioxide go over the original steady state value.
- because for the biomass the steady state value is not reached after the third step of the simulation (even after a step of 72 hours), it is difficult to see here if the biomass would fall under the original steady state value (as CO_2 has a greater value). A simulation of the change of the liquid input flow rate to 1ml/min on a column in steady state with the standard working condition (input of 2.8ml/min) has been made. It indicates that after 10 hours feeding at 1ml/min, the mean biomass concentration is 0.193 g/l (original concentration is 0.236 g/l) and *Nitrosomonas* represent only 69,0% of the total population (original ratio of 70.5%).

Six hours after the return to the standard processing conditions, all concentration values except CO_2, have reached their original steady state values. The fact that at the end of the simulation with an input flow rate of 1 ml/min, the biomass is near its original value, is probably the reason why biomass takes its original value again so quickly.

Nevertheless, it can be noted that the dissolved carbon dioxide will tend to reach its original steady state values.

It can be noted here that the oxygen profile (figure 15-c) is the same as the nitrifying efficiency profile (figure 15-g).

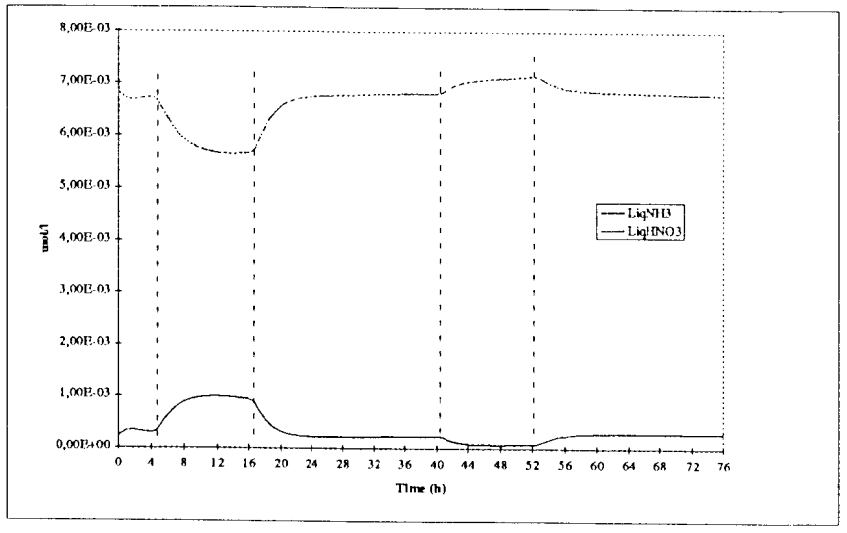


Figure 15a Flow rate variations - Evolution of NH3 and HNO3 concentrations in liquid outlet

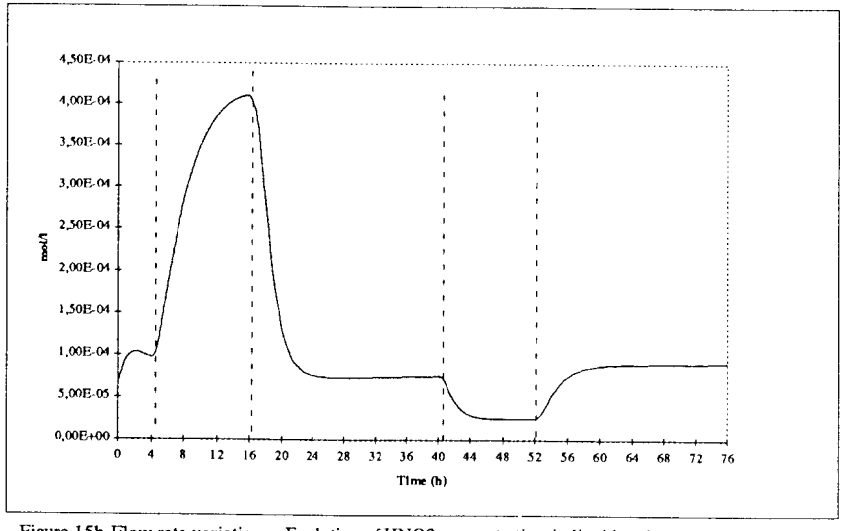


Figure 15b Flow rate variations - Evolution of HNO2 concentration in liquid outlet

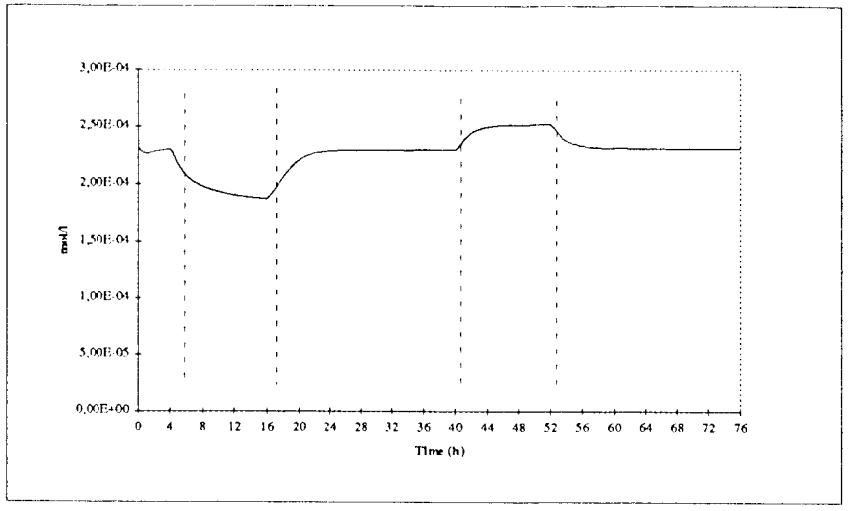


Figure 15c Flow rate variations - Evolution of the dissolved O2 concentration in liquid outlet

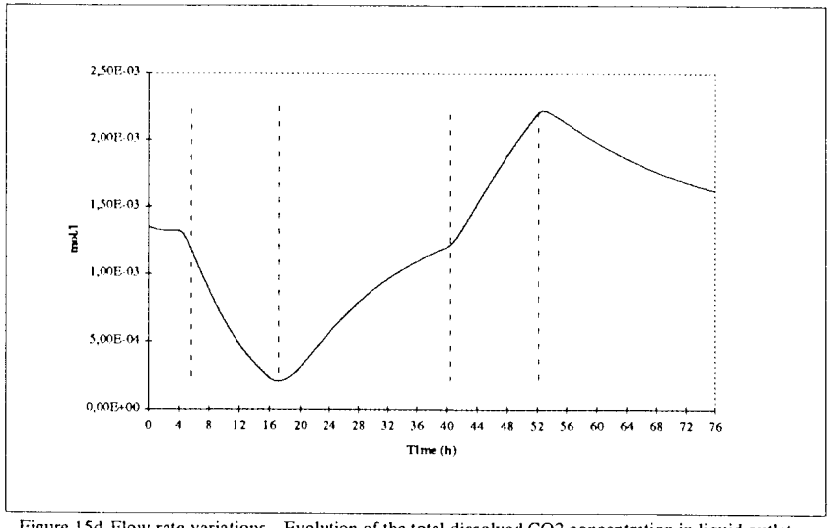


Figure 15d Flow rate variations - Evolution of the total dissolved CO2 concentration in liquid outlet

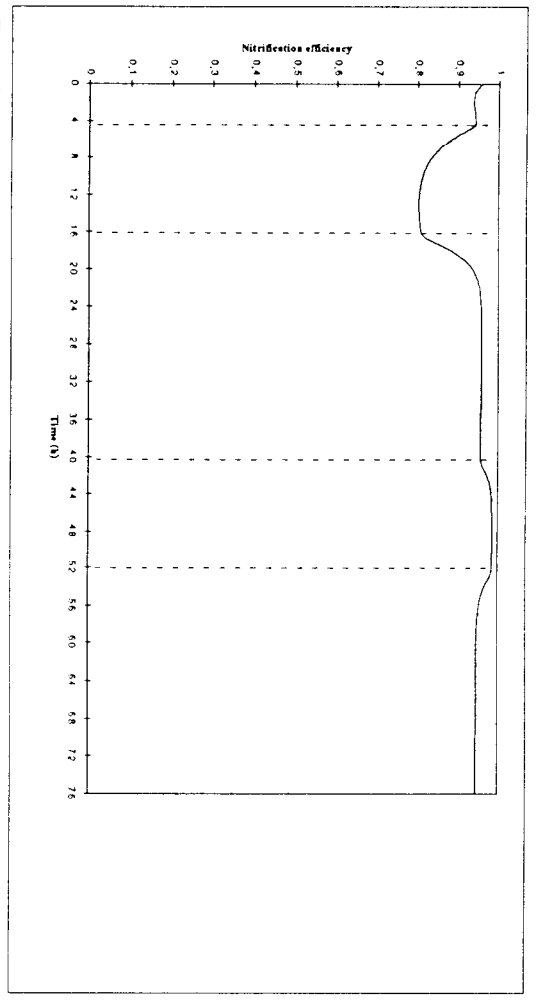


Figure 15e Flow rate variations - Evolution of the nitrifying efficiency

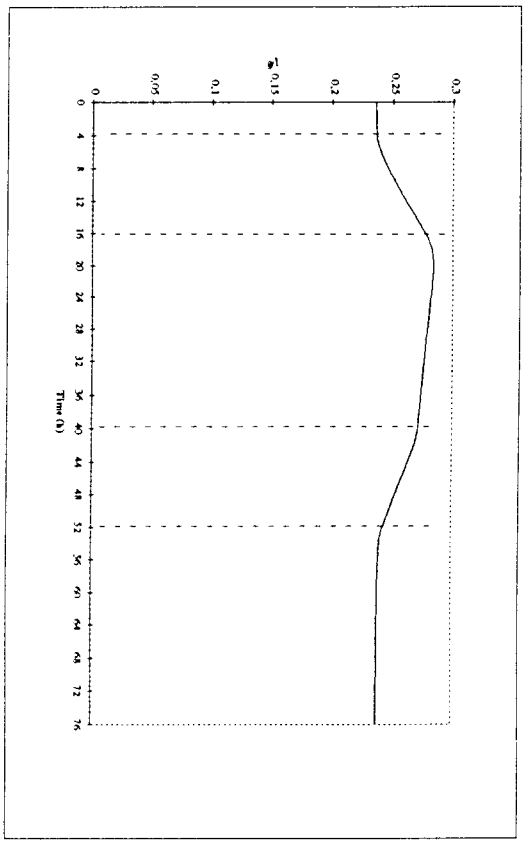


Figure 15f Flow rate variations - Evolution of the mean fixed biomass

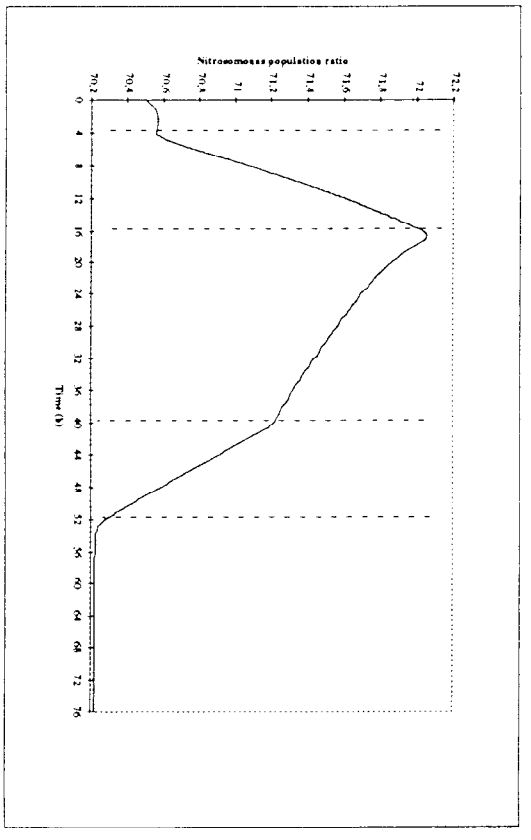


Figure 15f Flow rate variations - Evolution of the fixed Nitrosomonas population

3.2.3 - Input NH_3 concentration variations

A four steps process is simulated:

0-4 hour: standard inputs on the column (appendix A). N-NH_3 load of 0.11 kg/m^3.day

4-16 hour: NH3 concentration set to 200 N-NH_3 mg/l (i.e. N-NH_3 load of 0.22 kg/m^3.day; 14.28 mmol NH_3/l)

16-28 hour: NH3 concentration set to 400 N-NH_3 mg/l (i.e. N-NH_3 load of 0.44 kg/m^3.day; 28.56 mmol NH_3/l)

52-76 hour: standard inputs on the column are applied again: 100 N-NH_3 mg/l (i.e. N-NH_3 load of 0.11 kg/m^3.day; 7.14 mmol NH_3/l)

The results of the simulation are reported in figures 16 as bulk concentrations (NH_3, HNO_3, HNO_2, O_2, CO_2), mean biomass concentration, mean *Nitrosomonas* ratio inside the column, and the nitrifying efficiency of the process. Dashed lines separates the different steps.

When the input ammonia concentration is up to 2 times the original value of 100 mg/l, the outlet ammonia , nitrate and nitrite concentrations are increased. In order to analyse the effect of ammonia input variation, it is better to observe the nitrifying efficiency (figure 16-g).

The nitrifying efficiency falls to 87% and the profile for oxygen CO_2 and fixed biomass are comparable to the effects observed by increasing the input liquid flow rate. As previously, this is a response to a variation of the NH_3 load.

Increasing again the NH_3 input to 400 mg/l, greater increase the outlet concentrations of ammonia and nitrite, while the nitrification efficiency falls quite linearly. The increase of NH_3, reflects that there is not enough *Nitrosomonas* to oxidise ammonia. In the same way, the increase of nitrite concentration reflects that there is not enough *Nitrobacter* to oxidise the nitrites produced by *Nitrosomonas*. This is illustrated in figure 16-f, by the *Nitrosomonas* population, which represents 74% of the total fixed biomass, while the steady state value is about 70%. The growth rate of *Nitrosomonas* and *Nitrobacter* are too slow to respond to high variations of the NH_3 load applied on the column.

A carbon limitation appears near 24 hours of simulation.

[NOTE: the half saturation constant for HCO_3^- fixed at 10^{-10} mol/l has been changed in this simulation to 10^{-7} mol/l, due to computational time problems. This change only affect the CO_2 steady state value for the limitation, which is near 10^{-7} mol/l instead of 10^{-10} mol/l]

This limitation affects the nitrification:
- the nitrate and nitrite increase is reduced
- the ammonia increase is enhanced
- the growth of *Nitrosomonas* is more reduced than that of *Nitrobacter* (figure 16-f).
- the oxygen decrease is quite stopped (figure 16-c)

The limitation continues 8 hours after the return to the standard processing conditions (100 N-NH_3/l). The limitation disappears when the ammonia is completely exhausted (figure 16-a), i.e. when the growth is no more stimulated by the excess of NH_3.

After the CO_2 limitation, the oxygen, nitrite, ammonia concentrations and the nitrifying efficiency quickly return to the original steady state values. The nitrate, carbon dioxide and fixed biomass concentration need more than 24 hours to return to their original steady state values.

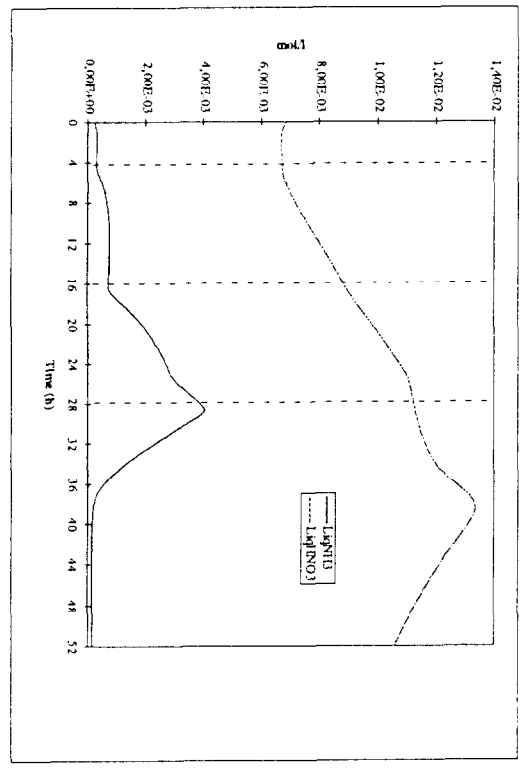


Figure 16a: [NH3] input variation - Evolution of NH3 an HNO3 concentrations in liquid outlet

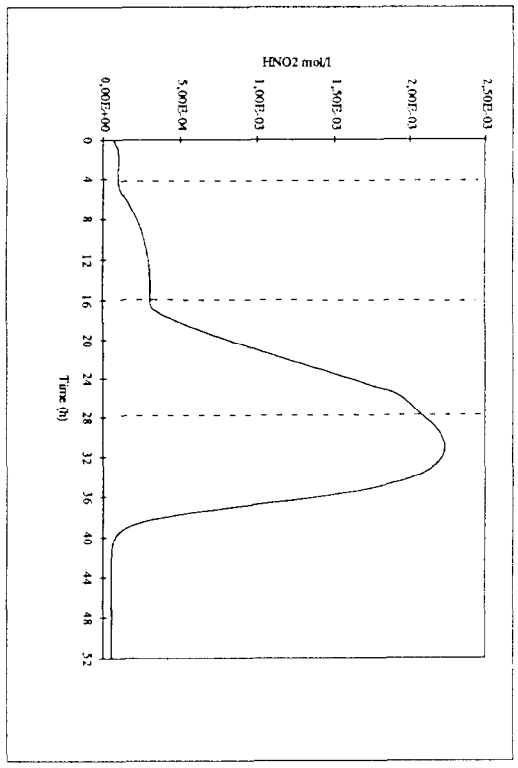


Figure 16b: [NH3] input variation - Evolution of HNO2 concentration in liquid outlet

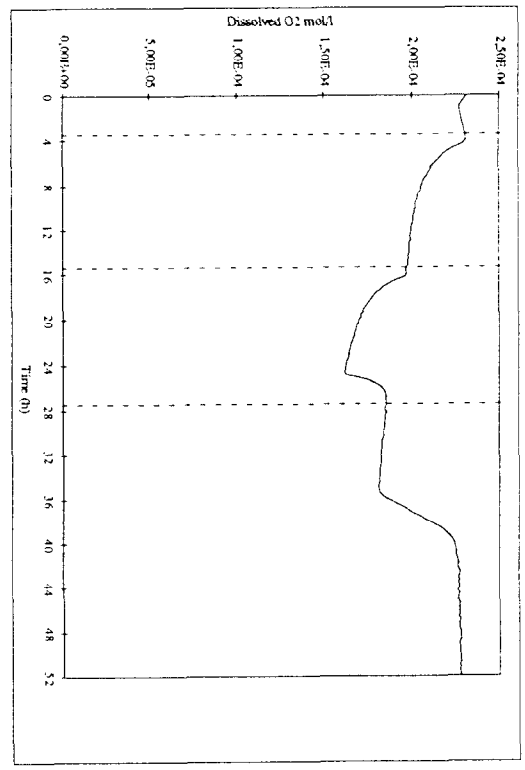


Figure 16c: [NH3] input variation - Evolution of dissolved O2 concentration in liquid outlet

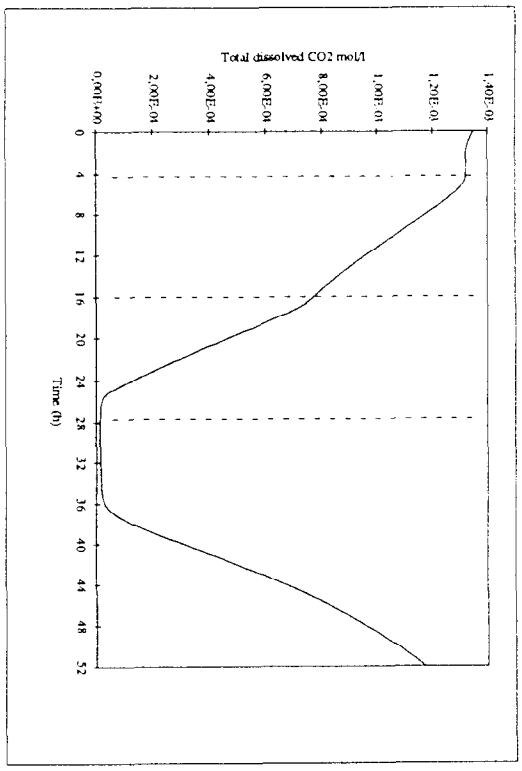


Figure 16d: [NH3] input variation - Evolution of total dissolved CO2 concentration in liquid outlet

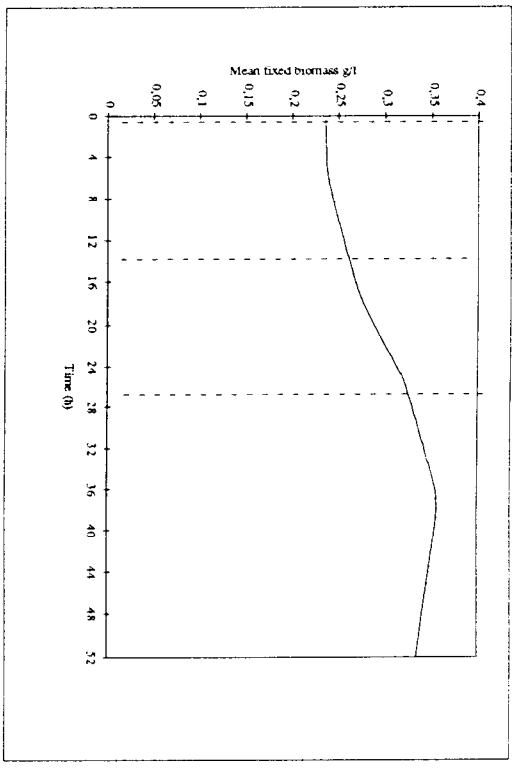


Figure 16c: [NH3] input variation - Evolution of the mean fixed biomass

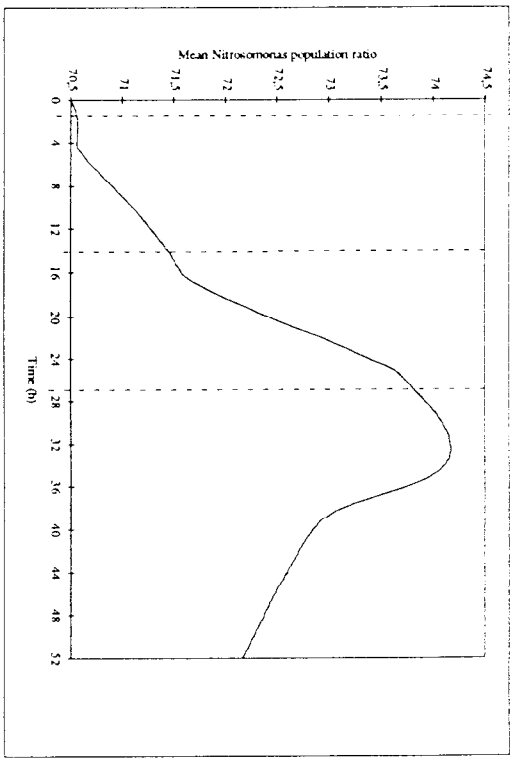


Figure 16d: [NH3] input variation - Evolution of the mean fixed Nitrosomonas population ratio

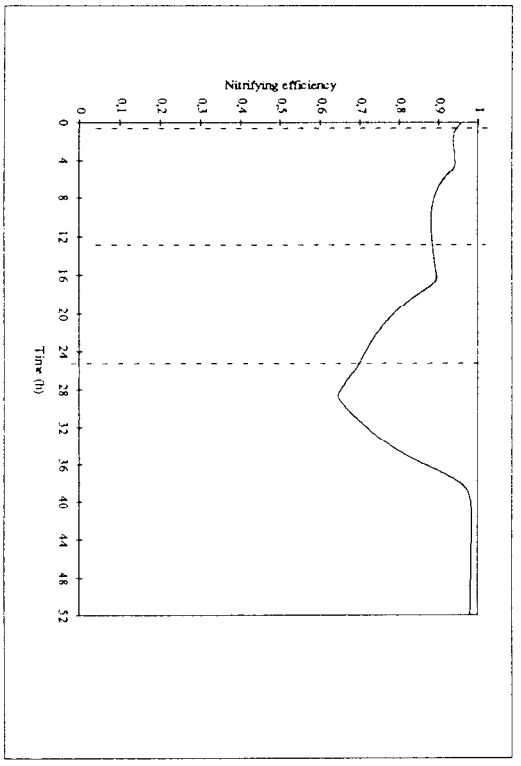


Figure 16e: [NH3] input variation - Evolution of the nitrifying efficiency

Conclusion

The previous model developed in TN27.1 and 27.2 was updated in order to introduce:
- the inhibitory effect of NO_2^- and NO_3^- on the Nitrobacter growth
- a biofilm diffusion model

Because in autotrophic nitrification the biofilm thickness is sufficiently thin to neglect the diffusion limitation, the biofilm model was not attached to the previous fixed bed column nitrifying model.

The sensitivity of the model to biological parameters (growth rates, maintenance coefficients, half saturation constants) was studied. The sensitivity is more important in short dynamics (when the steady state is not reached) than in long dynamics for which the steady state is reached.

For variation of the biological parameters in the range of 0.5 to 2 times their original value, the nitrifying efficiency in steady state situation was generally not changed of more than +/- 5%. The most sensible criteria are in every situation the ammonia and the nitrite concentrations, but the sensitivity must be compared with the low values of these concentrations.

The RTD analysis, first studied in TN 27.2, was continued. The flow parameters N (number of tanks used to represent the fixed bed), f (liquid back-mixing) and f' (gas back-mixing) were identified using UAB RTD experiments. It appears that N and f can not be simultaneously identified, because they are linearly dependents. A value of 155% for f has been determined when the fixed bed is assumed to be represented by 5 tanks in series.

For f', the gas back-mixing, because of the very short mean residence time of gases, it can be assumed to be equal to 0%.

The transient behaviour has been studied throughout 3 situations: an oxygen shutdown, a variation in input ammonia concentration and a variation in the input liquid flow rate.

the delay of about 1 hour observed between the action and its effects in the liquid outlet, is the time for the liquid to reach the top of the column from the bottom.

A peak of nitrite is observed when the growth of Nitrosomonas is enhanced (i.e. when ammonia oxidation is enhanced). The steady state population ratio of Nitrosomonas is about 70%. The variation in the nitrite concentration can be related to the variations in the ratio of the 2 population of micro-organisms.

For high ammonia load (0.44 kg/m3.h), the carbon source (CO_2) becomes limiting for the growth.

References

Boon B. and Laudelout H. (1962) "Kinetics of nitrite oxydation by *Nitrobacter winogradsky*" Biochem. J. N°85. pp 440-447.

Cox D. J., Bazin M. J. and Gull K. (1980)"Distribution of bacteria in a continuous-flow nitrification column" Soil Biol. Biochem. Vol.12. pp 241-246.

Forler (1992) " MELiSSA: Première étude du compartiment nitrificateur" CUST Clermont ferrand. ESA/YCL 1567/CF

Hunik J.H., Meijer M.L.C.and Tramper J. (1993) "Kinetics of *Nitrosomonas europea* at extreme substrate, product and salt concentrations". Appl. Microbiol. Biotech.. Vol. 37. pp 802-807.

Hunik J. H., Meijer H.J.G., and Tramper J. (1993b) "Kinetics of *Nitrobacter agilis* at extreme substrate, product and salt concentrations". Appl. Microbiol. Biotech.. Vol. 40. pp 442-448.

Hunik J. H., Bos C. G., den Hoogen M. P., De Gooijer C. D. and Tramper J. (1994)"Co-immobilized *Nitrosomonas europea* and *Nitrobacter agilis* cells: validation of a dynamic model for simultaneous substrate conversion and growth in K-carrageenan gel beads". Biotech. Bioeng. Vol. 43. pp 1153-1163.

Compounds involved in the model and their physico-chemical constants

Compound: non ionic form	first dissociated form	second dissociated form	third dissociated form	K_A (25°C)	k_i (25°C)
NH_3	NH_4^+			1.762 10^{-5} [TN 23.1.][c]	1.173 10^{-2} [TN 23.1.][c]
HNO_2	NO_2^-			3.98 10^{-4} *	
HNO_3	NO_3^-			Complete dissociation	
CO_2	HCO_3^-	CO_3^{2-}		4.320 10^{-7} [TN 17.1.]c 4.557 10^{-11} [TN 17.1.][c]	1635 [TN 17.1][c]
O_2					4.272 10^4 [TN 17.1][c]
H_3PO_4	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}	6.918 10^{-3} [TN 27.1.] 6.166 10^{-8} [TN 27.1.] 4.780 10^{-13} [TN 27.1.]	
H_2SO_4	HSO_4^-	SO_4^{2-}		Complete dissociation 1.047 10^{-2} [TN 27.1.]	
H_2O	OH^-			10^{-14}	Po=0.031 atm [c]
Biomass *Nitrosomonas*					
Biomass *Nitrobacter*					

[c]: calculated from a temperature dependent relation
*: updated from TN 23.2

Kinetic parameters

			Reference	Remarks
μ_{max}^{Ns}	$5.7\ 10^{-2}\ h^{-1}$		Hunik et al (1994)	mean values calculated
μ_{max}^{Nb}	$3.6\ 10^{-2}\ h^{-1}$		Hunik et al (1994)	from several
m^{Ns}	$3.38\ 10^{-3}$		Hunik et al (1994)	continuous cultures
m^{Nb}	$7.92\ 10^{-3}$		Hunik et al (1994)	
Limiting substrate	K^{Ns}	K^{Nb}		
NH_3	$6.625\ 10^{-5}$ mol/l	-	Hunik et al (1994)	Model parameter
NO_2^-	-	$3.6\ 10^{-4}$ mol/l	Hunik et al (1994)	values for a fixed bed
O_2	$5.05\ 10^{-6}$ mol/l	$1.7\ 10^{-5}$ mol/l	Hunik et al (1994)	of carragenan beads
HCO_3^-	10^{-10} mol/l	10^{-10} mol /l		no carbon limitation
Inhibitory substrate	I^{Ns}	I^{Nb}		
NO_2^-	-	0.557 mol/l *	Hunik et al (1992)	Model parameter
NO_3^-	-	0.188 mol/l *	Hunik et al (1992)	values
Substrate	$Y_{X/Si}^{Ns}$	$Y_{X/Si}^{Nb}$		g biomass / mol substrate Si Agebraic value
NH_3	-5.082	-115.566		
NO_2^-	5.316	-1.519		
NO_3^-		1.342		
O_2	-4.246	-3.539		
HCO_3^-	-23.0438	-23.0438		
HPO_4^{2-}	-2589.191	-2589.191		
SO_4^{2-}	-6583.943	-6583.943		
H^+	5.347	929.1854		
OH^-	23.044	23.0438		
	5.996	-46.894		
	$Y_{Smt/Si}^{Ns}$	$Y_{Smt/Si}^{Nb}$		mol maintenance substrate / mol Si Agebraic value
NH_3	-1			
NO_2^-	1	-1		
NO_3^-		1		
H_2O	1			
H+	1			
O_2	-0.5	-1.5		

*: updated from TN 23.2

Column design

Column:

Diameter: 120 mm.

Height: 716.2 mm occupied by beads + liquid + gas (calculated from the occupied volume of 8,1 l).

755 mm total (calculated from the total volume of 8.53 l)

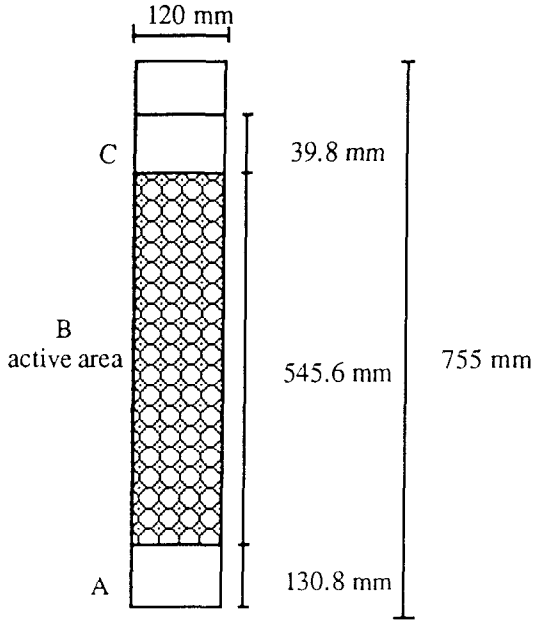
Volume: 8.1 l (experimental occupied volume measured at UAB Laboratory).

8.53 l (total volume calculated from the dimensions of the UAB column)

Void fraction ε^{col}: 0.52

Liquid void fraction $\varepsilon_L{}^{col}$: 0.475

Gas void fraction $\varepsilon_G{}^{col}$: 0.045



Part A

Volume: 1.48 l

Part B (active fixed bed area)

Volume: 6.17 l

ε: 0.37

ε_L: 0.33

ε_G:0.04

Part C

Volume: 0.45 l

Flow and design parameters for the standard configuration

Column	Height: 716.2 mm diameter:120 mm Volume part A:1.48 l Volume part B:0.45 l Pressure: 1 atm Temperature: 25°C
Fixed bed (active area)	Particle diameter: 4.1 mm N: 5 f: 0% f': 0%
Input flow rate	Fin: 2.8 ml/min Gin: 0.03 l/min
Recycling ratio	R_L: 6.42 R_G: 99
Gas composition	CO_2: 0.004% O_2: 21% H_2O: 0%
Liquid composition	NH_3: 7.14 mmol/l (100 mg N-NH_3/l) H_3PO_4: 0.1 mmol/l (no limiting) H2SO3: 0.1 mmol/l (no limiting)
Gas-Liquid transfer parameters	$K_La\|_{O2}$: 51 h^{-1} (0.014 s^{-1}) $K_La\|_{CO2}$: 51 h^{-1} (0.014 s^{-1}) $K_La\|_{H2O}$: 500 h^{-1} $K_La\|_{NH3}$: 0 h^{-1} (no gas-liquid transfer) [other parameters are defined in above]
Kinetics parameters	Kwo: 0% [other parameters are defined above]
Physico-chemical parameters	[parameters are defined above]
Biofilm	No biofilm limitation in standart configuration D_{O2}= 2.05 10^{-9} m^2 s^{-1} for biofilm concentrations calculation

Bulk phase concentrations

[mol/l - except biomass g/l]

Level in the column	NH3	HNO3	HNO2	CO2 tot	Dissolved O2	Water	H2SO4 tot	H3PO4 tot	Free Ns	Free Nb
Part A (bottom)	1,17E-03	5,92E-03	5,71E-05	1,28E-03	2,31E-04	55,56	1,00E-04	9,99E-05	0,00E+00	0,00E+00
Fixed bed - Tank 1	4,23E-04	6,52E-03	1,93E-04	1,29E-03	1,54E-04	55,56	9,99E-05	9,98E-05	0,00E+00	0,00E+00
Fixed bed - Tank 2	3,09E-04	6,71E-03	1,16E-04	1,32E-03	2,12E-04	55,56	9,99E-05	9,98E-05	0,00E+00	0,00E+00
Fixed bed - Tank 3	2,69E-04	6,78E-03	8,66E-05	1,33E-03	2,25E-04	55,56	1,00E-04	9,99E-05	0,00E+00	0,00E+00
Fixed bed - Tank 4	2,50E-04	6,82E-03	7,34E-05	1,34E-03	2,28E-04	55,56	1,00E-04	9,99E-05	0,00E+00	0,00E+00
Fixed bed - Tank 5	2,38E-04	6,83E-03	6,61E-05	1,35E-03	2,30E-04	55,56	1,00E-04	9,99E-05	0,00E+00	0,00E+00
Part C (top)	2,38E-04	6,83E-03	6,61E-05	1,35E-03	2,32E-04	55,56	1,00E-04	9,99E-05	0,00E+00	0,00E+00

Gas phase fraction

Level in the column	CO2	O2	Water
Part A (bottom)	9,11E-04	0,1784	3,08E-02
Fixed bed - Tank 1	9,06E-04	0,1781	3,08E-02
Fixed bed - Tank 2	9,03E-04	0,1781	3,08E-02
Fixed bed - Tank 3	9,01E-04	0,1781	3,08E-02
Fixed bed - Tank 4	9,00E-04	0,1781	3,08E-02
Fixed bed - Tank 5	9,00E-04	0,1781	3,08E-02
Part C (top)	8,99E-04	0,1781	3,08E-02

Fixed biomass

[g/l]

Level in the column	*Nitrosomonas*	*Nitrobacter*
Part A (bottom)	0,00E+00	0,00E+00
Fixed bed - Tank 1	0,621	0,1901
Fixed bed - Tank 2	0,122	8,50E-02
Fixed bed - Tank 3	4,70E-02	3,83E-02
Fixed bed - Tank 4	2,47E-02	2,09E-02
Fixed bed - Tank 5	1,53E-02	1,31E-02
Part C (top)	0,00E+00	0,00E+00

Biofilm thickness

[µm]

Level in the column	Biofilm	h lim O2	h for 02=0
Part A (bottom)	-	-	-
Fixed bed - Tank 1	1,09	9,287	27,861
Fixed bed - Tank 2	0,2781	12,24	36,72
Fixed bed - Tank 3	0,1146	13,44	40,32
Fixed bed - Tank 4	6,11E-02	14,03	42,09
Fixed bed - Tank 5	3,82E-02	14,39	43,17
Part C (top)	-	-	-

Heigth of the column

[m]

Level in the column	
Part A (bottom)	0,1309
Fixed bed - Tank 1	0,24
Fixed bed - Tank 2	0,3491
Fixed bed - Tank 3	0,4582
Fixed bed - Tank 4	0,5673
Fixed bed - Tank 5	0,6764
Part C (top)	0,7162

Values of the experimental data reported by UAB Laboratory (TN 25.330)

Time (min)	[BD] experiment 2 of UAB	Time (min)	[BD] experiment 3 of UAB
5	0.004	0	0
13	0.008	6	0.004136
16	0.112	10	0.08031
20	0.136	15	0.1203
25	0.165	20	0.1406
30	0.186	26	0.1675
35	0.200	30	0.1902
40	0.213	35	0.1986
47	0.225	40	0.2231
51	0.229	44	0.2312
55	0.234	51	0.2344
60	0.236	55	0.2365
65	0.238	60	0.2343
70	0.239	65	0.2379
75	0.237	70	0.2418
81	0.238	75	0.2423
86	0.236	80	0.2433
90	0.236	87	0.2463
95	0.238	90	0.2466
100	0.242	95	0.2441
119	0.239	120	0.242
133	0.235	135	0.2416
146	0.236	145	0.2351
159	0.232	160	0.2346
200	0.226	205	0.228
231	0.222	235	0.2216
278	0.211	260	0.2198
305	0.210	316	0.2103
700	0.160	750	0.1563
1092	0.125	960	0.1337
1122	0.123	1111	0.1218
1143	0.116	1205	0.1131
1153	0.115	1210	0.1183
1161	0.115	1215	0.1126
1191	0.109	1222	0.113
1215	0.110	1231	0.1119
1253	0.115	1238	0.1105
1279	0.106	1246	0.1093
1299	0.103	1275	0.1082
1309	0.103	1293	0.1065
1331	0.104	1313	0.1058
1340	0.104	1325	0.1043
1360	0.107	1403	0.09891
1387	0.102	1692	0.08103
1427	0.096	2361	0.05089
1870	0.068	2873	0.03574
2421	0.050		

Effects of inhibitory concentrations of nitrite and nitrate (TN 27.1)

	Nitrogen concentration mg ml^{-1}	Effect	Reference
Nitrosomonas			
Nitrite	1400	36% inhibition of oxygen uptake	Meyerhof (1916)
	4200	100% inhibition of oxygen uptake	
	500	Prolong lag at all pH value but no inhibition at alkaline pH	Lewis (1959) Pokallus (1963)
	2500	100% inhibition-lag	Lewis (1959)
		50% inhibition-lag	Pokallus (1963)
Nitrate	-	No effect recorded	
Nitrobacter			
Ammonia	12 mmol NH_4^+/l	50% inhibition ; pH 8	Gee et al. (1990)
	0.01 mmol NH_4^+/l	30% inhibition; pH 8	Aleem and Alexander (1960)
	0.072 mmol NH_4^+/l	50% inhibition; pH 7.4	Prakasam and Loer (1972)
Nitrite	40	No lag, no inhibition	Aleem and Alexander (1960)
	130	Prolonged lag 2-3 days	
	≤500	Added to exponentially growing culture - no effect	
	1400	40% inhibition due to undissocied nitrous acid	Boon and laudelout (1962)
	2226 (0.159 mol NO_2^-/l)	Value of non competitive inhibitory constant; pH 7.4	Hunik et al. (1992)
Nitrate	500	No effect	Aleem and Alexander (1960)
	1000-2000	Prolonged lag	
	5000	No nitrification	
	2000-5000	Added to active culture did not lead to significant depression NO3- accumulation does not interfere with NO2- oxidation	
		Greater inhibition with increase aeration	Gould and lees (1960)
	2632 (0.188 mol NO_3^-/l)	Value of non competitive inhibitory constant; pH 7.4	Hunik et al. (1992)

Reference not cited in TN27.1:

Gee C.S., Suidan MT, Pfeffer JT (1990) "Modelling of nitrification under substrate inhibiting conditions". J Env Eng 116. pp18-31.