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TECHNICAL NOTE 39.2

NitriSim validation

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CONTENT

T.N. 39.2: Nitrifying model: validation with experimental results

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Introduction

The purpose of this technical note is to simulate the bench nitrifying experiments performed at UAB.
The main objectives are

- to identify the hydrodynamic parameter values for the bench column in the N-tank in series model (i.e. number of tanks and back-mixing coefficient)
- to fit the steady-state experiments and the transient experiments by identifying if necessary the biological parameter values for Nitrosomonas and Nitrobacter

In a first part, the physical characterisation of the bench column for the simulation in NitriSim (dimensions, volumes, design), derived from the real column , is presented. The hydrodynamic parameters values were identified from liquid RTD experiments As a comparison, the current description of the pilot reactor is also presented.

In a second part, the simulations of experiments (steady-state and transient) are performed. The efforts were focused to the simulation of steady state experiments. The oxygen volumetric transfer coefficient (K_La) was identified as well as the biological maintenance coefficient in order to fit experiments.

I NitriSim update

For simulation of the experiments led by UAB with bench columns for the study of the nitrification process (TN 37.410; TN 37.510; TN 37.520) the NitriSim program was slightly modified from the previous version 2.4 (TN 32.2). These changes concern:

- the addition of a compound, namely inorganic carbon, in the input medium feeding the column. The medium used by UAB (TN 37.410) contains a bicarbonate source (0.8 g $NaHCO_3$) which is the carbon source for growth of the micro-organisms. Liquid CO_2 (including dissolved CO_2, HCO_3^- and CO_3^{2-}, the respective ratios of which depend on the pH) is considered in the definition of the liquid feed for the simulations.

- in order to be able to perform simulations of the columns in batch conditions (no liquid input flow rate and continuous recycling), the recycling of both gas and liquid phases was defined in term of flow rate instead of in term of ratio (recycling flow rate/input flow rate) as in the previous version of the software.

- the proposal of ADERSA for the reduction of computational time using a Laplace transform of the model (TN 35.2) was adopted.

All these modifications are included in the version 3.0 of NitriSim.

II Columns characteristics : from bench columns and pilot reactor to model

This part will detail and fix the values used to define the characteristics of the columns currently used for experiments in UAB.

II.1 Bench columns

II.1.1 Dimensions of bench columns

The set-up of the bench column was reported by Perez et al. in TN 37.510. The characteristics of the three parts of the column are reported in table 1. It must be outlined that part C (top part of the column) is enlarged (figure 1a). For NitriSim it was assumed that the diameter of the column is the same for every part (figure 1b). Then for the top of the column, the dimensions were adapted in order to have a diameter identical to those of parts A and B (table 1).

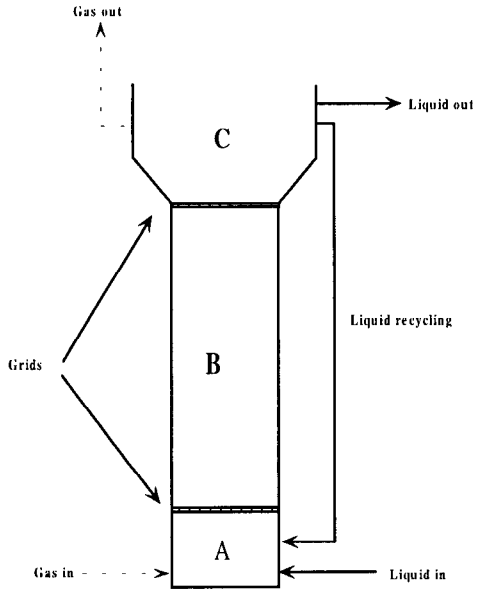

Figure 1a

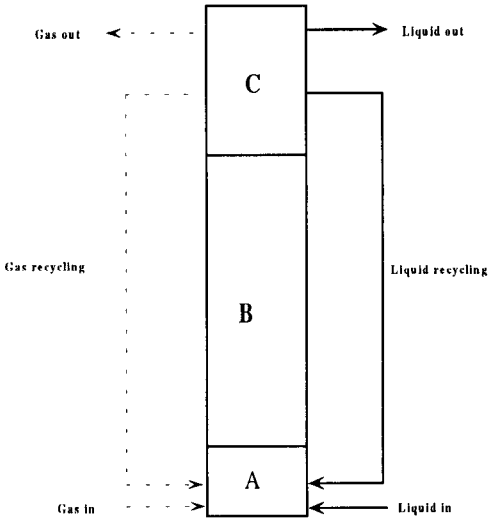

Figure1b

Figures 1: Schematic representations of the bench columns for experiments (a) and for modelling (b)

	Column dimensions (TN 37.510)			NitriSim column setup		
	Height (mm)	Diameter (mm)	Volume (ml)	Height (mm)	Diameter (mm)	Volume (ml)
Bottom Part A	79	38	89.5	50	38	89.6
Fixed bed Part B	267	38	302.7	267	38	302.7
Top Part C	22 20 30	38 38 to 78 78	24.9 52.8 143.3	203*	38	230.1
Grid x2	8	38	9.1			
Column			622.3	549	38*	622.3*

Table 1 : Dimensions of the bench column. Theoretical and NitriSim model.
* Sized to fit total theoretical volume

II.1.2 Voidage of the bed and hold-up

The total volume experimentally measured is 650 ml, and the solid volume is 138 ml (121 ml theoretically, and 130 ml if grids are included). Then, the voidage of the bed ε can be estimated to 0.57 using theoretical values. It must be outlined that this voidage becomes 0.55 if the experimental solid volume of 138 ml is used. These value must be compared with those of the pilot reactor, which are reported in section II.2.2.

Gas volume was measured for different gas flow rates, allowing the calculation of the gas volume fraction (ε_G) in the fixed bed (table 2). These parameters are required for the modelling of the column (TN 27.2), then the gas fraction in the column was derived from these reported values

Gas flow rate	Gas volume	ε (voidage of bed)	ε_G (gas fraction)	Hold-up %
15 ml/min	30 ml	0.55	0.032	6%
40 ml/min	40 ml	0.55	0.052	8%
500 ml/min	47 ml	0.55	0.054	9%

Table 2 : Voidage parameters for the bench columns

II.1.3 Hydrodynamic behaviour of the column

The experiments of residence time distribution in the liquid phase performed at UAB show a perfectly mixed tank behaviour (as for the pilot - report to II.2.3). This perfectly mixed behaviour results in fact from the high recycling flow rate (4.5 ml/min) compared to the low input flow rate (0.8333 ml/min).

II.1.3.1 Identification of hydrodynamic parameters

The RTD curves identified for different N-tank in series configuration (identification of liquid back-mixing parameter value) are reported in figures 3 for the 4 experiments leaded by UAB.
For experiments 3 and 4, the tracer was injected at the bottom of the fixed bed, instead of the bottom of the column (i.e. part A). This was taken into account in the simulations.
For experiments 1 and 2, best results for simulation were obtained by assuming the output tracer measurement was at the top of the fixed bed rather than in the top of the column (i.e. part C).

Several simulation were also performed by identifying other parameters such as

- a time lag due to difference in the time between the injection of tracer and the first measurement of tracer concentration at the output
- the liquid input flow rate
- the recycling flow rate

A better fit of experimental curves was obtained with these simulations, indicating that the hydrodynamic of bench column is quite sensitive to these parameters. As examples, the simulations for the experiments 1, 2 and 4 are respectively reported in figures 3e, 3f and 3g.
In figure 3f, there is a better fit of experiment 2 introducing a time lag for the first measurement.
In figure 3g, there is a better fit of experiment 4 changing the input liquid flow rate. In fact, the RTD simulations are sensitive to liquid mean residence time (V/F) leading to consider that either the liquid flow rates (input and recirculating flow rates) or the liquid volume inside the

fixed bed can be equivalently identified. Conversely, errors in the exact experimental determination of these 3 variables fully justifies identifying them in order to correctly take into account and to avoid a wrong identification of the other variables i.e. the back-mixing flow rate and the number of tanks.
In other words, the back-mixing coefficient must not have to compensate a mis-estimation of other variables in the model, even if they are supposed to be known.

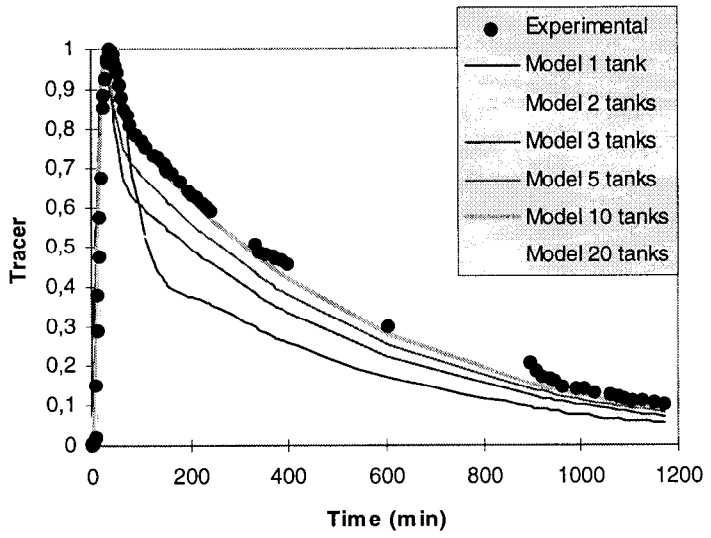

Figure 3a: RTD experiment 1 (TN 37.510). Simulated curve was fitted on experimental data varying the liquid back-mixing coefficient for a fixed number of tanks.
Operating conditions: Liquid input flow rate : 0.83 ml/min; Recycle liquid rate :4.5 ml/min; **Gas flow rate: 40 ml/min**

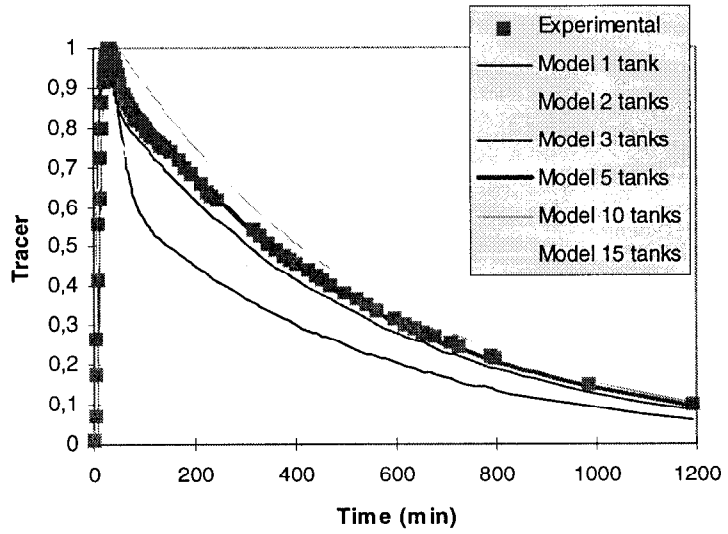

Figure 3b: RTD experiment 2 (TN 37.510). Simulated curve was fitted on experimental data varying the liquid back-mixing coefficient for a fixed number of tanks.
Operating conditions: Liquid input flow rate : 0.83 ml/min; Recycle liquid rate :4.5 ml/min; **Gas flow rate: 500 ml/min**

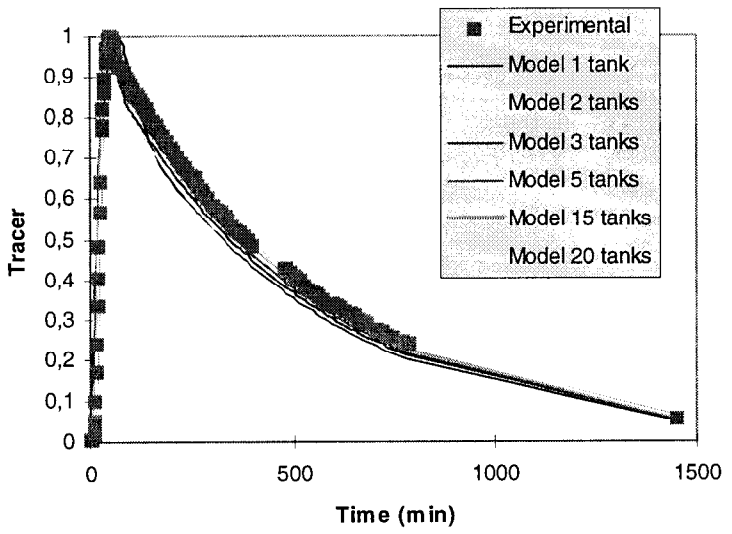

Figure 3c: RTD experiment 3 (TN 37.510). Simulated curve was fitted on experimental data varying the liquid back-mixing coefficient for a fixed number of tanks.
Operating conditions: Liquid input flow rate : 0.83 ml/min; Recycle liquid rate :4.5 ml/min; **Gas flow rate: 40 ml/min. Injection at the bottom of the fixed bed.**

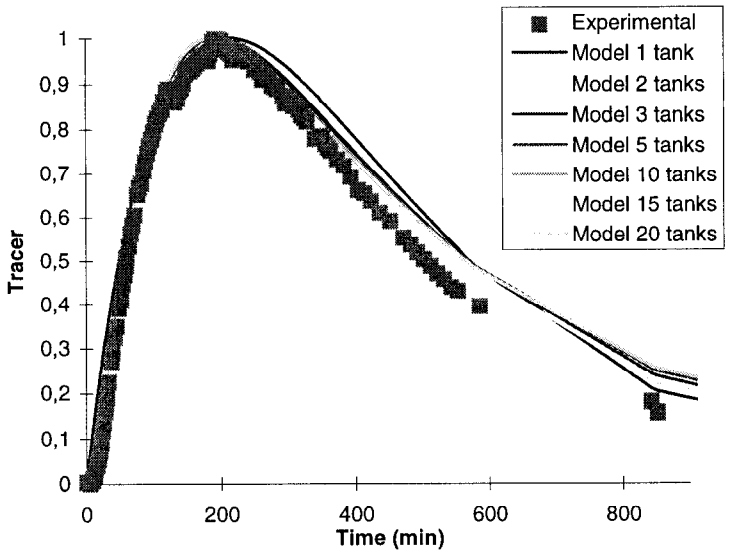

Figure 3d: RTD experiment 4 (TN 37.510). Simulated curve was fitted on experimental data varying the liquid back-mixing coefficient for a fixed number of tanks.
Operating conditions: Liquid input flow rate : 0.83 ml/min; Recycle liquid rate :0 ml/min; **Gas flow rate: 40 ml/min. Injection at the bottom of the fixed bed.**

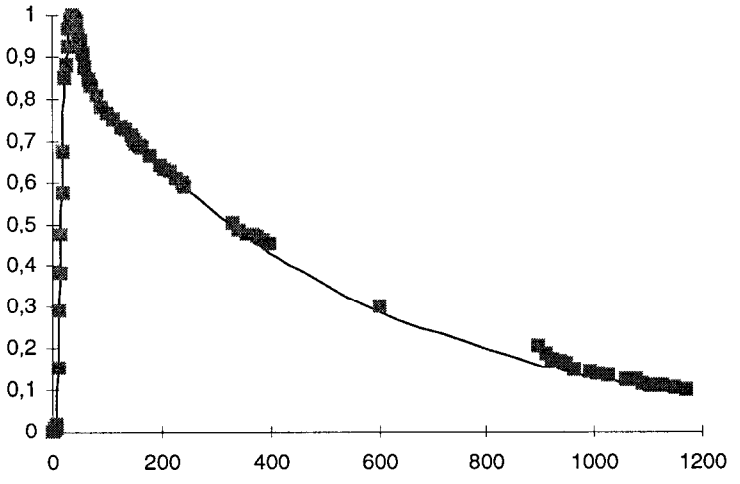

Figure 3e: RTD experiment 1 (TN 37.510). Simulated curve was fitted on experimental data.
Identification for 15 tanks gives :
Back-mixing : 8.43 ml/min
Start lag: 1.82 min
Liquid recirculation rate: 4.18 ml/min

Operating conditions: Liquid input flow rate : 0.83 ml/min; Recycle liquid rate :4.5 ml/min; Gas flow rate: 40 ml/min. Injection at the bottom of the fixed bed.

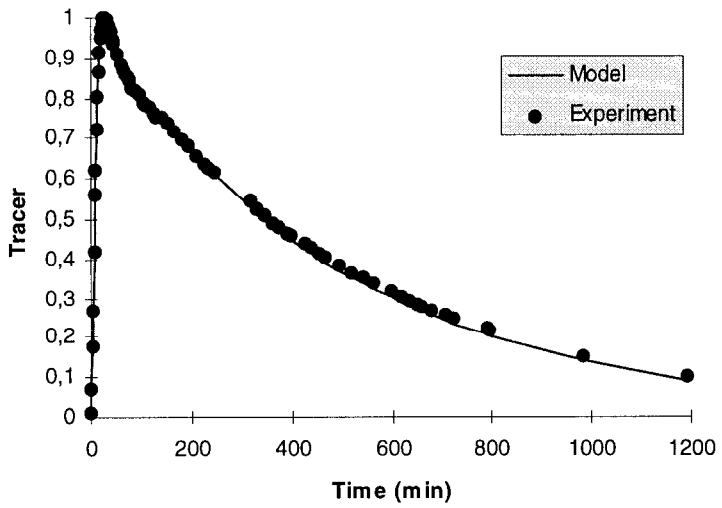

Figure 3f: RTD experiment 2 (TN 37.510). Simulated curve was fitted on experimental data.
Identification for 15 tanks gives :
Back-mixing : 8.9 ml/min
Start lag: 5.2 min

Operating conditions: Liquid input flow rate : 0.83 ml/min; Recycle liquid rate :4.5 ml/min; Gas flow rate: 500 ml/min. Injection at the bottom of the fixed bed.

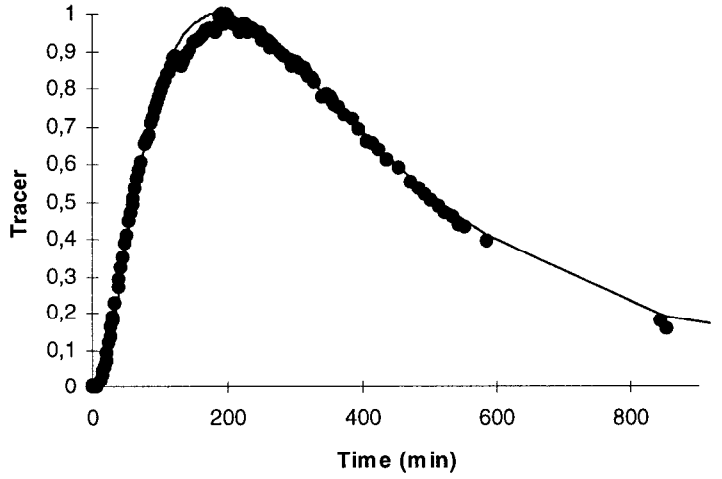

Figure 3g: RTD experiment 4 (TN 37.510). Simulated curve was fitted on experimental data.
Identification for 15 tanks gives :
Back-mixing : 9.44 ml/min
Liquid input : 1 ml/min

Operating conditions: Liquid input flow rate : 0.83 ml/min; Recycle liquid rate :0 ml/min; Gas flow rate: 40 ml/min. Injection at the bottom of the fixed bed.

The back-mixing flow-rates identified for experiments 1 to 4 (figures 3a to 3d), are reported in figures 4. For experiments 1, 3 and 4 which are performed for the same gas flow rate (40 ml/min), the values of the back-mixing flow rates are relatively close (figure 4a). In experiment 2, with a gas flow rate of 500 ml/min, the value are much higher (figure 4b).

It is difficult to observe a linear relationship between the back-mixing and the number of tanks as observed for the pilot reactor. Nevertheless it can be noticed that the minimum criteria obtained for the identification of the back-mixing parameter value in each experiment is obtained for quite the same back-mixing value (table 3a)

In table 3b are reported the results corresponding to the figure 3e, 3f and 3g where other parameters were identified simultaneously with the back-mixing coefficient. It illustrates the sensitivity of the back-mixing parameter value to the other hydrodynamic parameters. This is more marked with the experiment 2 which can be represented using the same parameters as for the other RTD experiments, assuming a time lag of 5.2 minutes. This time lag identified can also be interpreted as resulting from a bypass due to the high gas flow rate. The fact that

the peak of concentration is obtained at 28 minutes, while for a gas flow rate of 40 ml/in this peak is observed at 50 minutes is also in favour of this interpretation.

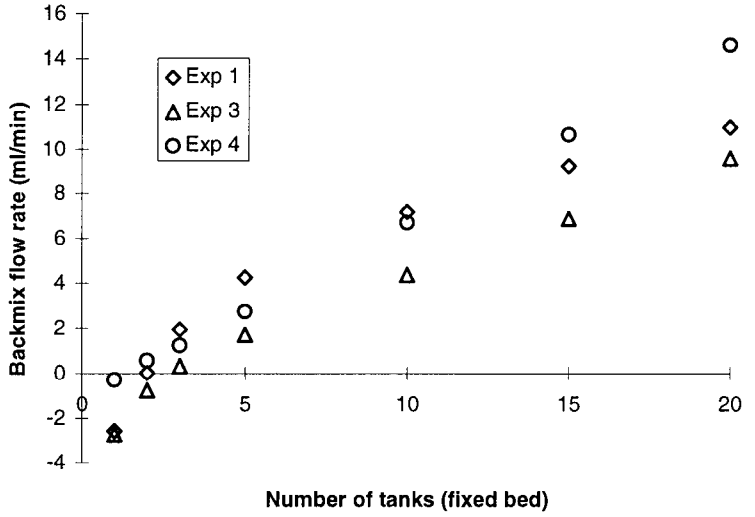

Figure 4a : Back-mixing flow rate identified as a function of the number of tanks.

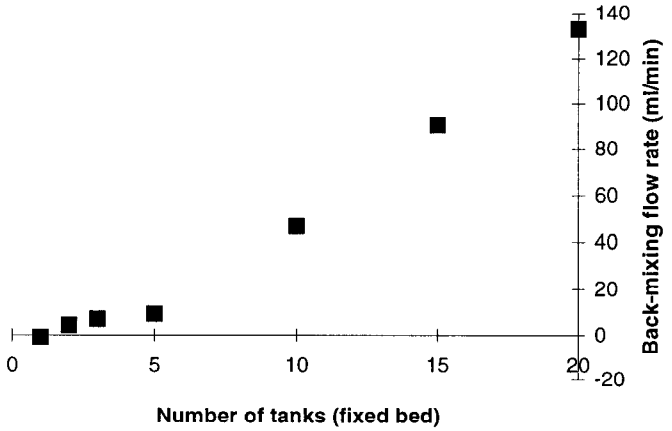

Figure 4b : Back-mixing flow rate identified as a function of the number of tanks.

Experiments	Number of tanks	Criteria	Back-mixing flow rate (ml/min)	Gas flow rate (ml/min)	Liquid flow rate (ml/min)	Recycling flow rate (ml/min)
Exp 1	15	2,11E-02	9,24	40	0,833	4,5
Exp 2	5	4.26E-02	9,25	500	0,833	4,5
Exp 3	15	1,69E-02	6,86	40	0,833	4,5
Exp 4	15	19.06E-02	10,65	40	0,833	0

Table 3a: Best results for each identification of back-mixing value for each experiment.

Experiments	Number of tanks	Criteria	Back-mixing flow rate (ml/min)	Time lag (min)	Liquid flow rate (ml/min)	Recycling flow rate (ml/min)
Exp1	15	$< 10^{-2}$	8.43	1.82	-	4.18
Exp 2	15	$< 10^{-2}$	8.9	5.2	-	-
Exp 4	15	$< 10^{-2}$	9.44	-	1	-

Table 3b: Simultaneous identification of several hydrodynamic parameters.

II.1.3.2 Conclusions and remarks for the bench columns hydrodynamic parameters
As seen in table 3, fitting the experimental RTD curve by identifying the back-mixing parameters gives close values of back-mixing, but different values of the number of tanks for different gas flow rates. It is important to take in mind at this point that the number of tanks cannot be changed during a simulation.

It must noticed that by identifying other parameters together with the back mixing flow rate gives:

- better curve fitting (better criteria)
- more homogenous identification results (figures 3e, 3f, 3g) as for 15 tanks for the fixed bed, for all RTD experiment a back-mixing parameter value ranging from 8.5 to 9.5 ml/min is calculated (table 3b).

The identification of back-mixing appears then relatively sensitive to the operating conditions (flow rates, recycling, time lag). Identification for various operating condition can be of interest to fix the hydrodynamic parameters.

At this point of the study, the configuration of 15 tanks and a back-mixing flow rate set to 9 ml/min seems reasonable. It must be kept in mind that it is important to avoid a too high value for back-mixing between the top the bottom and the fixed bed as this can greatly affect the oxygen transfer rate.

II.1.4 Gas liquid volumetric coefficient
The K_La values for oxygen were measured experimentally by UAB on bench column with and without a biofilm for different gas flow rates, stirring conditions and liquid recycle flow rates. Measurements were performed at the top of the column (part C). The results are compiled in table 4.

Remarks :
The effect of temperature seems low. The stirring effect is low (the measurements giving K_La are made at the top and the stirring paddle is at the bottom of the column). Nevertheless a variation of 7% of the K_La value can result in an important change in the efficiency of a column in limiting conditions.
The recycle liquid flow rate seems to have an influence (20%) on K_La value.

Without biofilm						
Air flow rate (ml/min)	Stirring (rpm)	Rec. flow (ml/min)	VVM (min^{-1})	Temperature (°C)	K_La (s^{-1})	K_La (h^{-1})
9	-	-	-	-	0.00046	1.66
15	-	-	-	-	0.0007	2.52
40	300	8	0.08	28	0.0013	4.68
40	300	16	0.08	-	0.0016	5.76
40	500	8	0.08		0.0014	5.04
100	300	8	0.2		0.0032	11.52
250	300	8	0.05		0.0072	25.92
500	300	8	1.0		0.0120	43.2

With biofilm						
Air flow rate (ml/min)	Stirring (rpm)	Rec. flow (ml/min)	VVM (min^{-1})	Temperature (°C)	K_La (s^{-1})	K_La (h^{-1})
40				28	0.0019	6.84
40				24	0.0016	5.76
250				28	0.0054	19.44

Table 4 : K_La on the bench column (from UAB). TN 43.410

II.2 Pilot reactor

II.2.1 Dimensions of the pilot reactor

The set-up of the bench column was reported by Perez et al. in TN 25.330. The characteristics of the three parts of the column are reported in table 5. As can be seen on figures 5, there is a greater concordance between the model design and the pilot design than between the model design and the bench column design.

	Column dimensions (TN 25.330)			NitriSim column setup		
	Height (mm)	Diameter (mm)	Volume (l)	Height (mm)	Diameter (mm)	Volume (ml)
Bottom Part A	150	112	1.48	131	120	1.48
Fixed bed Part B	493 63	120 112	5.58 0.62	548	120	6.20
Top Part C	86	112	0.89	78 *37.2 [exp]*	120	0.88 *0.42 [exp]*
Grid x2	-	-	-			
Column	796		8.56	757 *716.2 [exp]*	120	8.56 *8.1 [exp]*

Table 5 : Characteristics of the pilot reactor. Theoretical and NitriSim model. [exp] is for the value calculated from experimental volume measurement in the column. The experimental value measured at UAB was 8.1 Liters. This corresponds to a part C filled with 0.46 L. These dimensions of the 8.1 Liters filled column will be used to perform the simulations (TN 27.2 and 27.3).

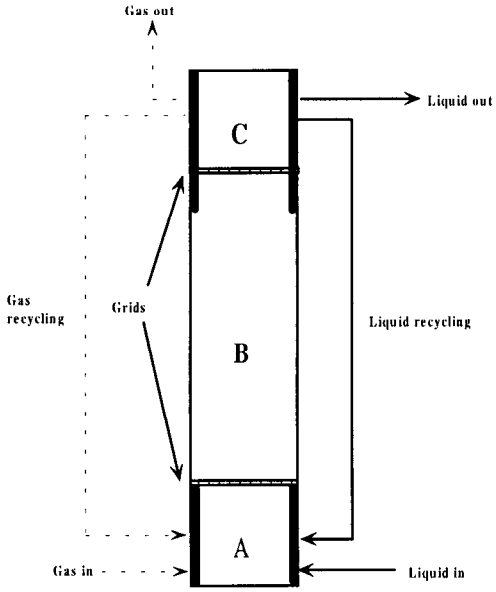

Figure 5a

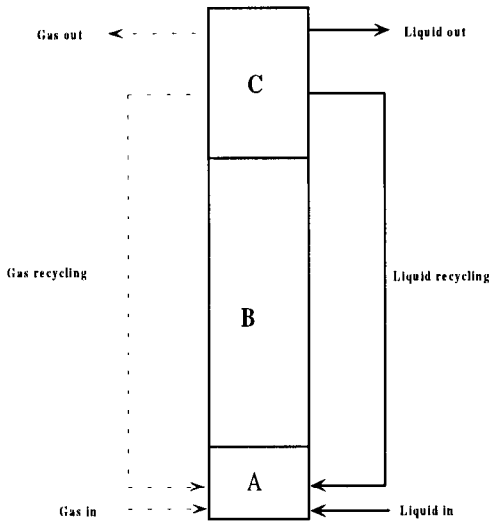

Figure 5b

Figures 5: Schematic representations of the pilot for experiments (a) and for modelling (b)

II.2.2 Voidage of the bed and hold-up

A determination of the gas hold-up and of the gas fraction in the pilot reactor was performed by Perez et al. (TN 25.330 - table 6). The solid volume measured by Perez et al. was 3.9 L, what gives (reported to the 6.2 L of the part B) a voidage ε of 0.37. It must be remarked that this value is very different from the value of 0.48 calculated by Forler (ESA-X-997 , 1994), and from the values calculated for bench columns.

Gas flow rate	Gas volume	ε (voidage of bed)	ε_G gas fraction	Hold-up
3L/min	400 ml	0.371	0.0952	4.9%

Table 6 : Voidage parameters for the pilot column

II.2.3 Hydrodynamic behaviour of the column

In previous technical notes concerning the modelling of the nitrifying column (TN 27.2; TN 27.3), the choice of the hydrodynamic model (i.e. N the number of tanks for the fixed bed and f the back-mixing coefficient) was discussed.

First identifications were performed from liquid RTD experiments on the 8 Liters pilot reactor. It was shown that liquid has a perfectly mixed behaviour in the column (when the liquid recirculation exists).

As a consequence, it was shown that the two parameters N (number of tanks) and f (back-mixing ratio) are coupled.

It appears from the previous simulation results that each of the 3 hydrodynamic parameters of the model can be taken as a characteristic of one of the phase of the column.

- the number of tanks N characterises the biomass behaviour inside the column. As biomass is fixed, N describes the axial dispersion of the biomass in the bed and then the heterogeneity of the biomass distribution in the bed.
- the liquid and the gas back-mixing terms enable to describe the axial dispersions of liquid and gas in the bed, which are higher than the one of the biomass (perfectly mixed behaviour of the liquid phase). Note that, as the residence time of gas is very short (a few minutes) compared to that of liquid, the back-mixing of gas can be neglected.

II.2.4 Gas liquid volumetric coefficient

For the 8 Liters column reactor, a K_La value varying from 51 h^{-1} to 86 h^{-1} was measured in the top and in the bottom of the column, depending on the stirring rate (at the bottom of the column) and on the gas flow rate (TN 25.330).

The air flow rate on the pilot reactor (3 to 5 L/min) gives VVM values from 0.8 to 1.4, which are ten times higher than those used for bench columns.

III Simulations of the bench columns experiments

Simulations of the bench columns were performed using NitriSim v3.0. The objectives are :

- to simulate the steady state behaviour of the bench columns in various operating conditions
- to simulate the transient behaviour of the bench column

In order to fit experiments and simulations the biological parameters will be identified.

III.1 Model parameters for NitriSim

The biological coefficients (stoichiometric yields, growth rates and maintenance rates) used and listed in the previous studies of NitriSim were taken in a first trial (TN 27.3).

The physical coefficients (gas-liquid equilibrium constants, acid-base equilibrium constants) were conserved too (TN 27.3). The setting point values of pH and temperature were used as fixed values in the model (i.e. pH=8.1 and T=30°C)
In a first approach, it was then assumed that the biological and the physical constants were independent of the process and of the process operating conditions.

III.2 Bench column in steady state

III.2.1 Experiments
The nitrifying performance of the bench column in different operating conditions were reported by Perez et al. (TN 37.520 ; TN 43.410).

It can be noticed in table 7 that the increase in the air flow rate slightly increases the ammonia oxidation. The effect on nitrite oxidation is less significant. This is quite surprising because it suggests that ammonia oxidation is oxygen limited. But the Ks_{O2} constant for *Nitrosomonas* in the biological model is 10 times lower than for *Nitrobacter*, then normally oxygen limitation would appear first for *Nitrobacter* (nitrite oxidation), what seems not to be the case.

The operation of the bench column near the oxygen limiting conditions is confirmed by the results for a lower residence time (5 h) for which the removal efficiency is 67%.

It can be remarked that the results for identical operating conditions in experiments M6 and M6' are slightly different. Results of M6' were obtained for a column working for a longer time.

		NH_3 (g N/l)	Nitrite (g N/l)	Nitrate (g N/l)	Total nitrogen	Input ($N\text{-}NH_3$/l)	$N\text{-}NH_3$/L.h
M1	RT = 5 h 40 ml air/min	-	**15.7%**	**67.1 %**	-	0.3	-
M2	RT = 5 h 100 ml air/min	-	**5.3%**	**70.8 %**	-	0.3	-
M3	DR=0.075h^{-1} RT=13 h 9 ml air/min	0.44 (± 0.010) **14.52%** 14.67%*	0.008 (± 0.003) **2.64%** 2.67% *	0.251 (± 0.010) **82.84%** 83.67% *	0.303 (± 0.019) 101.00%% *	0.3	0.0225
M4	DR=0.075h^{-1} RT=13 h 9 ml air/min	0.58 (± 0.010) **15.10%** 14.50%*	0.03 (± 0.004) **7.81%** 7.50%% *	0.296 (± 0.007) **77.08%** 74.00% *	0.384 (± 0.014) 96% *	0.4	0.030
M5	DR=0.075h^{-1} RT=13 h 15 ml air/min	0.25 (± 0.006) **7.9%** 8.3% *	0.5 (± 0.003) **1.6%** 1.7% *	0.287 (± 0.010) **90.5%** 95.7% *	0.317 (± 0.019) 105.7% *	0.3	0.0225
M6	DR=0.1h^{-1} RT=10 h 40 ml air/min	0.013 (± 0.007) **4.3%** 4.3% *	0.007 (± 0.007) **1.3%** 1.3% *	0.285 (± 0.010) **93.4%** 95% *	0.305 (± 0.024) 101.7% *	0.3	0.03
M6'	DR=0.1h^{-1} RT=10 h 40 ml air/min		0.3%	99.7%		0.3	
M7	RT = 10 h 100 ml air/min	-	**0.3%**	**99.7 %**	-	0.3	-

Table 7: Nitrifying performance of the bench columns (Perez et al. TN 37.520; TN 43.410). * Calculation based on input concentration.

III.2.2 Simulations

The simulations of bench columns for steady-state were performed with NitriSim 3.0.

III.2.2.1 Hydrodynamic parameters

The number of tanks chosen for the fixed bed was 15 for all operating conditions, according to the results obtained with liquid RTD experiments.

The liquid back-mixing flow rate for each operating condition was set to 9 ml/min as it was the most relevant value identified on RTD curves for a number of tanks of 15.

III.2.2.2 The problem of gas-liquid transfer coefficient for oxygen

It was first observed that with the K_La values measured at the top of the column, it was impossible to obtain the nitrification efficiencies calculated in experiments: the oxygen consumption for N-oxidation (r_{O2}^{Tot}) is always greater than the maximum of oxygen that could be transferred (K_La . C*). The simulation performed with the K_La values measured are then far to fit experimental efficiencies. The correction of K_La, according to UAB, by taking into account the variation of the gas superficial velocity between the measurement area and the different part of the column have been included in NitriSim. Measured and corrected values of K_La for different operating conditions of the bench columns are reported in table 8.

	RT (h)	Flow gaz (ml/min)	**KLa mes (h^{-1})**	**KLa corr (h^{-1})**
M1	5	40	**4,7**	**35.9**
M2	5	100	**11,52**	**88.2**
M3	13,3	9	**1,6**	**12.7**
M4	13,3	9	**1,6**	**12.7**
M5	13,3	15	**4,7**	**19.3**
M6	10	40	**4,7**	**35.9**
M7	10	100	**11,52**	**88.2**

Table 8 : K_La values measured and corrected with the variation of superficial gas velocity (in the bed)

For the simulations, the corrected values of K_La (inside the fixed bed) were used. A theoretical oxygen consumption rate can be calculated from the production rate of nitrite and nitrate:

$$r_{O2}^{Tot} = 1 \cdot r_{NO2}^{Tot} + 1.5 \cdot r_{NO3}^{Tot} \text{ (mol/l.h)}$$

The accuracy for the K_La value used in simulation can be estimated by comparing experimental and simulated oxygen consumption rates. For simulation of experiments M1 to M7, results are reported in figure 6.

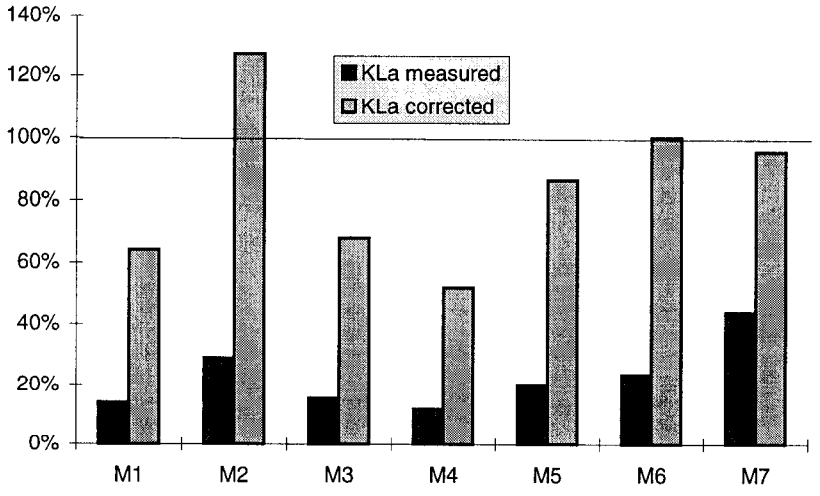

Figure 6 : Percentage of oxygen consumption rate calculated by simulations compared to experiments (for K_La values measured and corrected).

With the K_La value measured at the top of the column, r_{O2}^{Tot} is largely insufficient to allow the nitrification yields observed in experiments.
The correction of K_La value using the correlation proposed by UAB give better results but remains for some of the experiment also insufficient to allow the nitrification yields observed.

It must be noticed that for experiment M3 and M4, which are performed in the same operating conditions (excepted higher NH_3 input concentration for M4) it is surprising to have a

different r_{O2}^{Tot}, suggesting a higher K_La value for the column in experiment M4. But in principle, the 2 experiments must have the same K_La value.

III.2.3 An estimation for K_La in the fixed bed to fit experimental steady state values

It was seen that the first problems encountered are related to the value of K_La which was calculated using a relation very sensible to the precision of the measurement (it can be seen in table 4, measured K_La is quite sensible to gas and liquid flow rate and to stirring) and to the voidage calculated for the fixed bed.

The voidage chosen can be a great factor of discrepancy in the calculation of K_La using correction based of superficial gas velocity. In section II-1-2, two values of ε could be calculated, moreover, UAB states that the voidage varies with biofilm maturation.

As without a sufficient oxygen transfer rate it is impossible to be able to simulate the experiments, it is necessary to try to fit steady-state experiments by identifying the K_La values

III.2.3.1 Identification of K_La value to fit experiments

The identification of a K_La value inside the bed was tried with a simplex method in order to fit simulated and experimental r_{O2}^{Tot} values for the steady-state experiments M1 to M7. Convergence is assumed when K_La variation to fit experiments are less than 1%. This identification is only possible if it is assumed that the experiments occurs in limiting oxygen operating conditions. For this reason, the K_La of experiment M7 is not identified.

The K_La values identified for the fixed bed are reported in table 9. It must be noted that the K_La values at the top and at the bottom were kept constant at the measured values (including the correction for the K_La at the bottom of the column).

Experiment	Measured	Corrected (bed)	**Identified (bed)**
M1	4.7	35.9	**67**
M2	11.52	88.2	**56**
M3	1.65	12.7	**23**
M4	1.65	12.7	**34**
M5	2.52	19.3	**24**
M6	4.7	35.9	**36**
M7	11.52	88.2	-

Table 9: Measured, corrected and identified values for K_La (in h^{-1}) inside the fixed bed.

Important Notes:

1) The identification of K_La by this way is very sensitive to the operating conditions used to simulate the processes. Then, error in the estimation of flow rates (gas and liquid) and other hydrodynamic parameters can lead to important variations in the value of K_La identified. More generally, the accuracy of the K_La value is of the same order of magnitude of the accuracy of the liquid flow rate (i.e. ammonia load) in oxygen limiting conditions.
2) The effect of a possible limitation by diffusion inside a biofilm is not taken into account in the model. But if such a phenomena exists, it can perhaps explain the variation of K_LA values identified with the changes in the ammonia load.

III.2.3.2 Correlation for an estimation of the K_La in bench columns

It was tried to find a relation or a correlation between the K_La values identified and the operating conditions (gas and liquid flow rates). In figures 7a and 7b are plotted the K_La values respectively as a function of the liquid residence time and of the gas flow rates. It can be seen that it is difficult to observe a relation between K_La and each of these operating parameters.

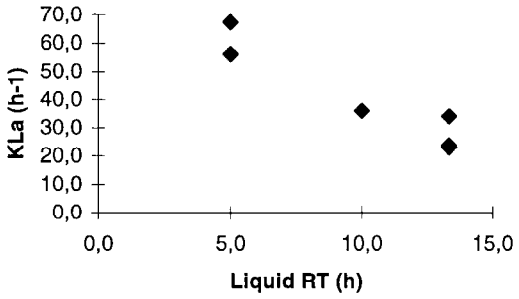

Figure 7a: K_La identified and liquid residence time.

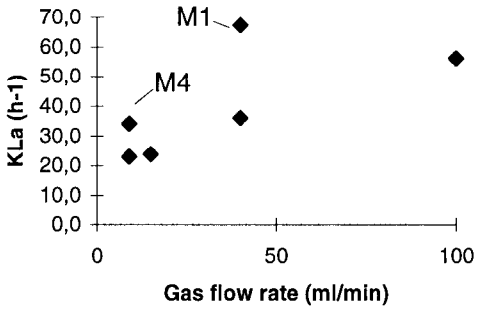

Figure 7b: K_La identified and gas flow rate.

The values identified for experiments M1 (67 h^{-1}) and M4 (34 h^{-1}) are high considering the operating condition and the other K_La value identified.

A good correlation can be obtained by:

$$K_La=a + b .Gin + c RT$$

with RT states for the liquid residence time (h), and Gin the gas flow rate (ml/min)

Variable	Value	Standard Error
a	104.14	4.03
b	-0.187	0.034
c	-5.92	0.296

This 2 independent variables correlation is obtained with a too small set of points (5 points) to be validated. This correlation gives also a higher weight for liquid RT than for gas flow rate. Using this correlation gives for experiment M7 a K_La value of 26.2 h^{-1}. But in order to have at least the same N-oxidation efficiencies as in experiments, it is necessary to have a value at least around 36 h^{-1}.

III.2.4 Nitrification yields

Now that the experimental and the model oxygen consumption rates are comparable, the nitrification yields measured in steady-state, i.e. the output concentration of each N-compounds can be compared with the simulations results.

III.2.4.1 Nitrification yields with the K_La values identified

The nitrification yields obtained using the value identified for the K_La are reported in table 10. It can be observed that the ratio of each species are different in the simulations and in the experiments. The total concentration of the N-compounds at the output of the column represent around 98% of the inputs, what is always lower than the quantities obtained in experiments.

	Experimental			Simulation		
	ammonia	nitrite	nitrate	ammonia	nitrite	nitrate
M1	17%	15,70%	67%	3.56%	63.08%	33.35%
M2	24%	5,30%	70,80%	3.58%	79.64%	16.78%
M3	14,52%	2,64%	82,84%	3.46%	37.46%	59.08%
M4	15,10%	7,81%	77,08%	2.55%	49.26%	48.19%
M5	7,89%	1,58%	90,54%	3.13%	9.75%	87.11%
M6	4,26%	2,30%	93,44%	2.08%	0.84%	97.08%
M7	0%	0,30%	99,70%			

Table 10 : N-oxidation efficiencies (output percentage of N-compounds) for experiments and simulations. The biological parameters used are those defined in previous technical notes.

III.2.4.2 Identification of the biological maintenance coefficients on experiment M5

The difference between simulation and experiment for the N-oxidation efficiencies, considering that the required oxygen is transferred, can be a consequence of biological reactions.

In steady state, the main biological parameters involved in our model are:

- the maintenance coefficients of *Nitrosomonas* and *Nitrobacter*, respectively
  $m_{ns}= 3.38\ 10^{-3}$ mol/g biomass. h
  $m_{nb}= 7.92\ 10^{-3}$ mol/g biomass. h

- the saturation constants for ammonia, nitrite and oxygen

The maintenance coefficient is the most sensible one affecting the N-oxidation efficiencies. By grinding the maintenance coefficients of *Nitrosomonas* and *Nitrobacter*, values have been estimated in order to fit the results obtained in experiment M5. These values are:

$m_{ns}= 8.6\ 10^{-3}$ mol/g biomass. h
$m_{nb}= 5.1\ 10^{-3}$ mol/g biomass. h

These new parameters values will replace the old one. The results obtained using these new maintenance parameter values are presented in the following section.

III.2.4.3 Nitrification yields : Simulation vs. experiments

In figures 8 the output concentrations obtained for the simulation of the 7 steady-state experiments (M1-M7) are reported using the K_La values and the maintenance coefficient identified.

In table 11 are reported the absolute deviation (i.e. %Simulation - %Experiment) and the relative deviation (i.e. $\frac{\%Simulation - \%Experimental}{\%Experiment}$) of the simulations vs. the experiments.

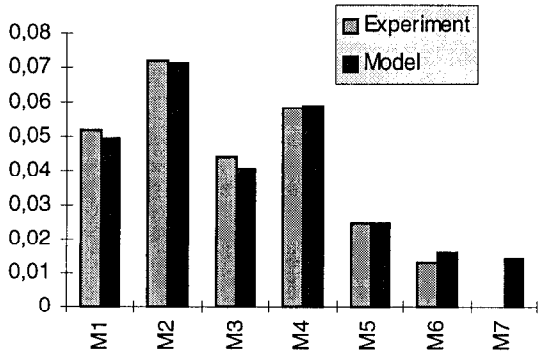

Figure 8a : Comparison between simulated and measured ammonia output concentration (g N/l) for steady state operating conditions, with identified values of K_La (table 9) inside the fixed bed.

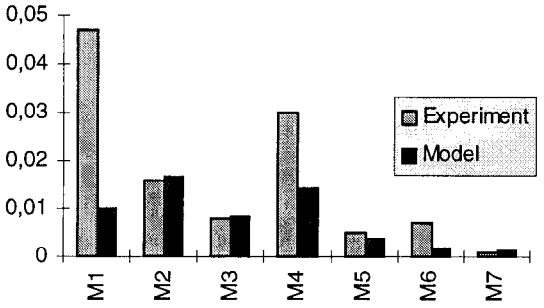

Figure 8b : Comparison between simulated and measured nitrite output concentration (g N/l) for steady state operating conditions, with identified values of K_La (table 9) inside the fixed bed.

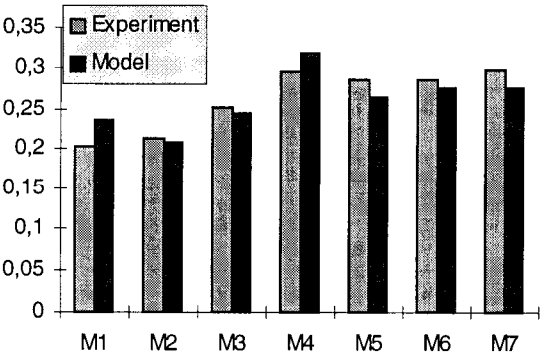

Figure 8c : Comparison between simulated and measured nitrate output concentration (g N/l) for steady state operating conditions, with identified values of K_La (table 9) inside the fixed bed.

	Absolute deviation			Relative deviation		
	ammonia	nitrite	nitrate	ammonia	nitrite	nitrate
M1	-0.55%	-12.26%	12.81%	-3.2%	-78.1%	19.1%
M2	0.26%	0.35%	-0.61%	1.1%	6.7%	-0.9%
M3	-0.77%	0.24%	0.53%	-5.3%	9.0%	0.6%
M4	-0.11%	-4.21%	4.32%	-0.7%	-53.9%	5.6%
M5	0.52%	-0.26%	-0.26%	6.5%	-16.3%	-0.3%
M6	1.25%	-1.78%	0.53%	29.3%	-77.4%	0.6%
M7	4.86%	0.10%	-4.96%	INF	31.8%	-5.0%

Table 11 : deviation of simulation to experiments. Absolute deviation = %Simulation - %Experiment. Relative deviation = $\frac{\%Simulation - \%Experimental}{\%Experiment}$

Note : For experiment M7, a K_La value of 36 h^{-1} is used. This is the minimal value required to obtained the results presented in figures 8 and table 11.

The experiments with which the most important deviations are observed are also those for which remarks have been made for the K_La values identified namely M1 and M4.
For experiment M7, such a complete nitrification (99.7 % of nitrate) was never obtained with the model, what explain the deviation for ammonia and nitrate).

III.2.5 Conclusion for simulation of bench column in steady state.
It appears that some difficulties were encountered in simulation of the steady-state behaviour of the bench nitrifying columns. Most of the problems can be linked to the difficulty to represent adequately the hydrodynamic behaviour of the column and/or the oxygen volumetric transfer rate coefficient.

The process itself seems not completely in steady-state, as for experiments M4 and M6', the N-oxidation is more efficient than for respectively experiments M3 and M6 performed in the same operating conditions. At this point it can be asked wether the biofilm, which is neglected in the current model, cannot have an influence.

Nevertheless preliminary results in steady state seems to indicate that the maintenance coefficients of *Nitrosomonas* and *Nitrobacter* are quite different from those previously used. As the biological parameters are independent of the kind of reactor used, the new values estimated for maintenance can be used in future simulations of the pilot reactor.
K_La value can be identified in order to fit experiments. The value identified are very different from the measured values and the corrected ones..

III.3 Bench column and transient operations

The 2 experiments reported in TN 43.410 were simulated:

- M6-M1: From the steady state of M6, the dilution rate is changed (from RT=10h to RT=5h), for a gas flow rate of 40 ml/min
- M7-M2: From the steady state of M7, the dilution rate is changed (from RT=10h to RT=5h), for a gas flow rate of 40 ml/min

III.3.1Simulation of M6'-M1
As it was seen previously, the steady-state behaviour for experiment M1 cannot be fully obtained. Moreover the K_La value required to have a N-oxidation comparable with the experiment is high (67 h^{-1}) compared to the other values calculated (36h^{-1} for M6). But the change in the liquid flow rate, seems too low to justify a change in the K_La value from 36 h^{-1} to 67 h^{-1}.
Another problem is that the steady state reported for the experiment M6' is different of this of experiment M6, what is perhaps an effect of the maturation of column.

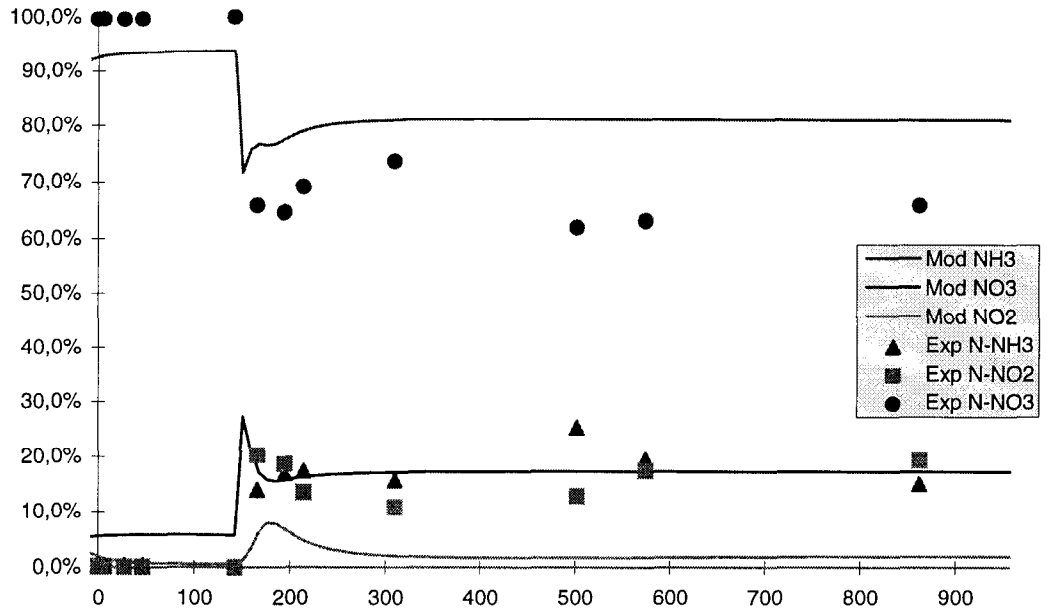

Figure 9 : Simulation of transient dynamic M6-M1 for the bench column.

III.3.2 Simulation of M7-M2

The simulation reported in figure 10 was performed for a 15-tank fixed bed. According to the results obtained in the previous analyses of steady-states, the K_La value inside the bed used was 36 h^{-1} for a gas flow rate of 100ml/min, and the maintenance coefficients were those previously calculated.

As can be seen in figure 10, the nitrite peak cannot be correctly simulated. It was tried to obtain better results by modifying the specific growth rate of the organisms, but without significant success.

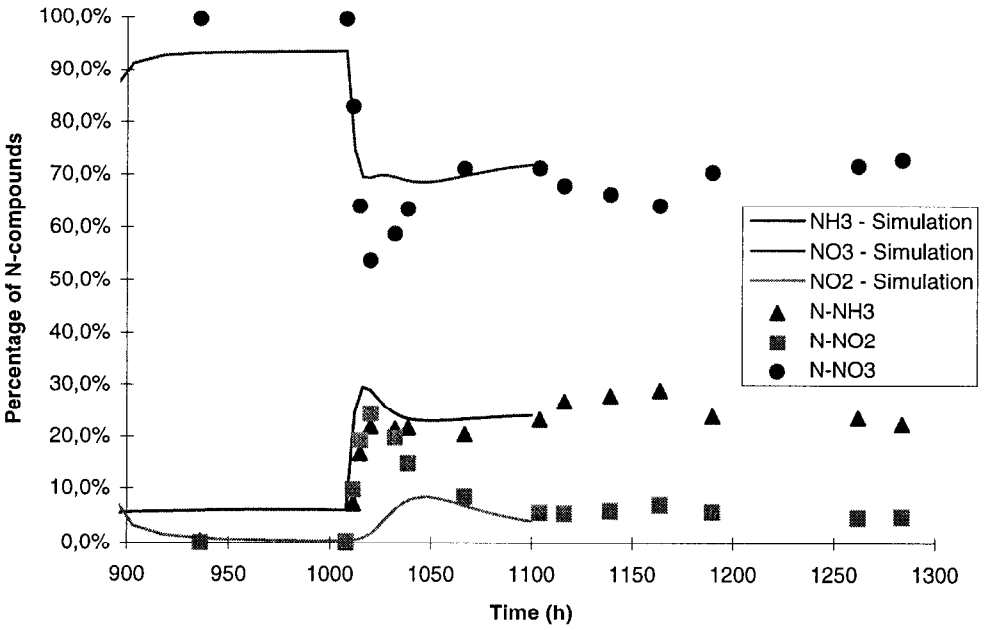

Figure 10 : Simulation of transient dynamic behaviour M7-M2 for the bench column.

At the present time, 2 possibilities are considered to explain the nitrite peak when the liquid flow rate is increased:

- the *Nitrosomonas* biomass is higher than this calculated in steady-state for experiment M7. Then for a rapid ammonia load increase, the biomass can quickly oxidise ammonia to nitrite. But this high *Nitrosomonas* biomass concentration cannot be obtained with our model. It can be also wondered if the biofilm diffusion limitation can play a role.
- the second possibility is an inaccurate representation of the hydrodynamic of the column.

Conclusion

The results of the simulation of the bench column experiments are mitigated. On one hand some problems have been encountered which are not completely solved at the present time, and which can appears also with the pilot reactor.

- First, the identification of RTD parameters (namely the liquid back-mixing parameter as a function of the number of tanks for the representation of the fixed bed), can be done. Nevertheless, some RTD experiments, as well as results obtained for transient operating conditions, suggest the N-tanks in series with back-mixing model is not well adapted to the bench columns dynamics, and that stagnant or by-pass can exist in the columns. This could be in accordance with the model of a plug-flow with stagnant zone used to represent a fixed bed column by Beg et al. (1996).
- A second problem concerned the determination of the K_La value for the fixed bed part of the column. It is easy to note that the K_La measured at the top of the column is not representative of the totality of the column. The correction based upon the gas superficial velocity inside the different part of the column allows to calculated K_La value which theoretically permits the N-oxidation at the rate observed in experiments. But using this correction gives sometime a K_La value always too low for the N-oxidation or too high, giving an N-oxidation greater than this observed. For this reason, the K_La inside the fixed bed has been calculated in order to fit experiments in steady-state. The values identified cannot be correlated. It is important to notice that the value identified are very dependant on the hydrodynamic description of the column that was chosen for the simulation (i.e. number of tanks and back-mixing parameter values).

These problems have not been encountered with the first test performed with the results obtained on the pilot reactor, probably because the pilot reactor was not operated near the oxygen limiting conditions as the bench columns. To solve the problems, changes in the hydrodynamic model can be envisaged.

Despite these difficulties, the steady-state of 6 of the 7 experiments reported by UAB have been successfully simulated. This has be done by identifying the biological maintenance coefficient for both *Nitrosomonas* and *Nitrobacter*.

At the present time the simulation of transient operating conditions is not satisfying. That can be probably linked with the problems for modelling hydrodynamics.

References

Beg S.A., Hassan M.M. and Naqvi M.S.M. Hydrodynamics and mass transfer in a cocurrent packed column. A theoretical study. The Chem. Eng. J. 63, 93-103, 1996.