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LGCB

MELiSSA

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TECHNICAL NOTE 55.2

K_La measurement in fixed bed columns

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Content

I Introduction

In previous studies (TN 39.2), some difficulties have been encountered for the validation of the model for the third MELiSSA compartment (nitrifying compartment). Two kinds of problems (perhaps linked together) were identified :

- The first was the identification of the liquid RTD parameters. The experimental RTD in bench columns suggest a more complex hydrodynamic than the N-tank in series with back-mixing. This is probably also linked to the small size of the bench columns knowing that such problems do not seem appear for the 8 Liter pilot column.
- The second kind of problem was the determination of the $K_L a$ in the fixed bed itself. The fixed bed is not directly accessible and the gas/liquid mixing at the bottom and at the top of the column (which represent more than half of the column liquid volume for bench columns) mask the gas transfer inside the bed.

It must be outlined that the activity of nitrifying strains (*Nitrobacter*, *Nitrosomonas*) is primarily dependent of gas-liquid exchange coefficients in the fixed bed section of the column reactor. Previous experimental studies have shown that the assessment gas-liquid transfer coefficient ($K_L a$) and mixing parameters as well was very difficult to obtain using the entire bioreactor due to the influence of top and sections.
It was therefore decided to perform specific study focussed on the characterisation of the fixed bed part.

In the present technical note:
- The test columns which have been built for this study are presented. The two test columns have been specifically designed and assembled with the aim of eliminating top and bottom sections and to perform only physical parameters studies.

- The $K_L a$ was measured for several gas flow rates by a gas balance technique coupled with sulphite method. The $K_L a$ were determined from experimental results and using the NitriSim model. The SimLab, "MatLab Toolbox" developed at LGCB, was used for simulation and identification of parameters. The toolbox includes the NITRISIM software previously detailed (TN 27.1, 27.2, 27.3 and 39.2). The measured values were also compared with literature predictive models.

II LGCB columns

II.1 LGCB Fixed bed columns

This part describes the characteristics of the two fixed bed columns designed at LGCB. Differences with the nitrifying columns are outlined. At the present time only the C50 column is on operation.

II.1.1 Overall characteristics

Two columns (called column C50 and column C150) were assembled in order to be able to operate in a large range of gas and liquid flows conditions . The characteristics of the columns are reported in Table 1. The values given in Table 1 are the specifications used to build the columns. The final characteristic can be slightly different (i.e. height of 1.01 m instead of 1 m). A more accurate sizing description for the column C50 is given in Table 6**.**

As can be seen in Table 1, the columns were designed in order to be complementary for the range of gas and liquid flow rates that can be used for nitrifying columns. Superficial gas velocity and liquid residence time of the UAB bench and pilot columns were used as the base for the choice of the flow rates applied on the LGCB columns.

	Liquid RT (h)	Gas superficial velocity (m/s)
8 Liters pilot column	1.5 – 2	0.011 – 0.02
Bench columns (including recycling flows)	0.29 – 0.32	0.0002 (low flow rates) 0.0002 – 0.0015 (nitrifying flow rates) 0.013 (highest flow rates)

Flow characteristic of UAB nitrifying columns (concern the fixed bed part – also called part B of columns)

Compared to the nitrifying columns (Bench and 8 liter pilot) 4 mains differences must be outlined :

- The LGCB columns have not the top and bottom volumes of the nitrifying columns. Then, the behaviour of the fixed bed zone can be only observed, which is the objective of this study.

- The LGCB columns are filled with glass bead instead of Biostyr® beads. This will avoid the problems of deformation of the beads (TN 47.2) which can affect the hydrodynamic of the column. Avoiding distortion of the hydrodynamic due to bead deformation, the comparison of the behaviour of the columns for different operating conditions would be more consistent. Nevertheless it will be necessary to performed experiment with Biostyr® beads also in future studies.

- The LGCB columns are higher than the fixed bed of the bench and the pilot nitrifying column, for a comparable diameter. That enables to improve gas/liquid exchange phenomena without impairing the quality of the results.

- The LGCB columns do not require a recycling of gas or liquid, but the flow rates used for feeding the columns are comparable to those of the nitrifying ones (in their bed part). This will reduce the perfect mixing effect due to the recycling, with the conservation of the same flow rates as those used in nitrifying columns.

II.1.2 Sampling and probes points

The height of the LGCB columns allows the addition of points for accessing the fixed bed (sampling or installation of probes). This could be useful in case of experiments for the study of profiles in the columns. The 5 points chosen are (Table 1):

     1 at the bottom of the column
     1 at ¼ of the height of the column
     1 at ½ of the height of the column
     2 at the top of the column

II.1.3 Hold_up measurement on the columns

The columns can operate in two modes (Figure 1).

- In one mode a part is added to the top of the column. The hold up can then be measured, enabling to calculate the volumes occupied (i.e. the voidage of the bed) by liquid and gas for fixed flow rates (Figure 1-A). It must be noticed that hold-up is therefore measured without liquid circulation.

- In a second mode this additional part is removed and behaviour of the fixed bed can be studied (Figure 1-B).
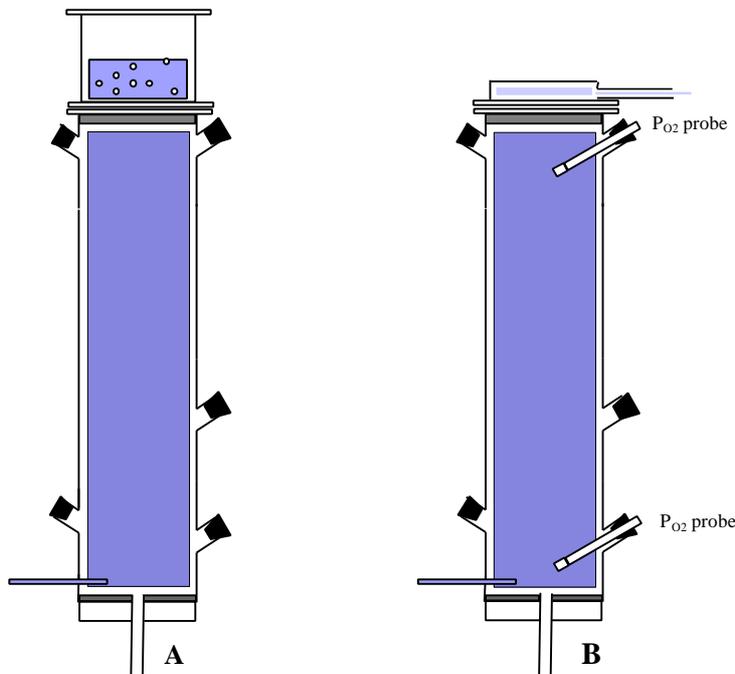
Figure 1 : Operating the columns.
A) Open column and additional top part : Hold-up measurement
B) Closed column : study of the fixed bed (hydrodynamic; Gas/liquid transfer….)

II.1.4 Gas and liquid feed of the columns

As for the UAB columns, LGCB columns are fed at the bottom both for gas and liquid (ascendant co-current columns).

For gas, instead of a gas sparger system with stirring, a porous plate (PORAL® IK 10-30-03) is used. Liquid feed is above the porous plate, at the center of the column (Figure 2). This system would allow a good dispersion of gas in liquid, enabling bubbles of very small size (order of 0.1 mm).This will probably affect both the hydrodynamic for gas and the mass transfer between phases.
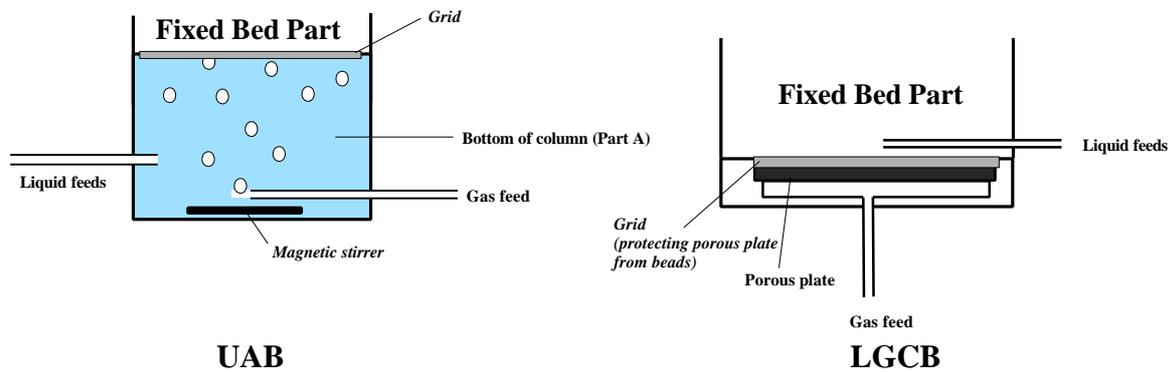
Figure 2 : Feeding systems of the UAB nitrifying columns and LGCB fixed bed column

II.1.5 Gas and liquid separation at the column output.

As the LGCB columns lack of part C of nitrifying column for the separation of gas and liquid phases, a gas/liquid separation system is added at the output of the columns (Figure 3). This separator is supposed to minimise the gas/liquid transfer effect leading to observe exclusively the gas/liquid transfer inside the fixed bed section.
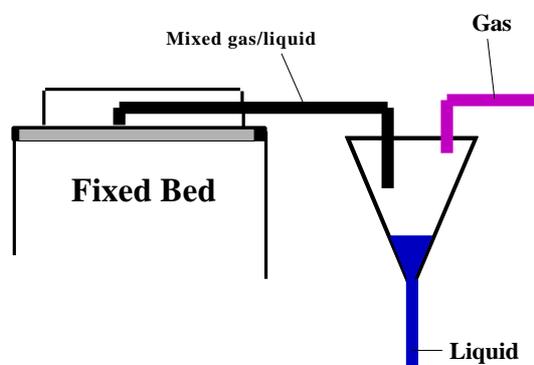
Figure 3 : Gas/liquid output separator on LGCB columns

	Column C50	**Column C150**

	Heigth : 1m
	Diameter : 50 mm
	Total volume : 1.96 L
	Section : 19.63 10^{-4} m^2
	
	Glass beads diameter : 4mm
	
	Characteristic dimension :
	D/d : 12.5
	
	Liquid flows:
	Flows rates : 0 – *10* L/h
	RT : 0.07 h minimum
	   *(Assuming a voidage of 0.34
	   and column filled by liquid)*
	
	Gas flows :
	Flows rates : 0.05 – 1 L/min
	Vo max : 0.0249 m/s
	   (Assuming a voidage of 0.34)
		Heigth : 1m
		Diameter : 150 mm
		Total volume : 17.67 L
		Section : 176.7 10^{-4} m^2
		
		Glass beads diameter : 4mm
		
		Characteristic dimension :
		D/d : 37.5
		
		Liquid flows:
		Flows rates : 0 – *10* L/h
		RT : 0.6 h minimum
		   *(Assuming a voidage of 0.34
		   and column filled by liquid)*
		
		Gas flows :
		Flows rates : 0.05 –30 L/min
		Vo max : 0.083 m/s
		   *(Assuming a voidage of
		0.34)*

Column : PVC Porous plate : inox , PORAL® IK 10-30-03 Beads : Glass bead (4 mm diameter) PolyLabo Ref. 12953.	**Complementarity of the columns** Liquid RT (h): C50 : 0.06 ------------------- inf C150 : 0.6 -------------------------------inf Vo Gas (m/s) C50 : 0.001-------------0.025 C150 : 0.0001 --- 0.083	

Table 1 : Detailed scheme of the two LGCB columns.
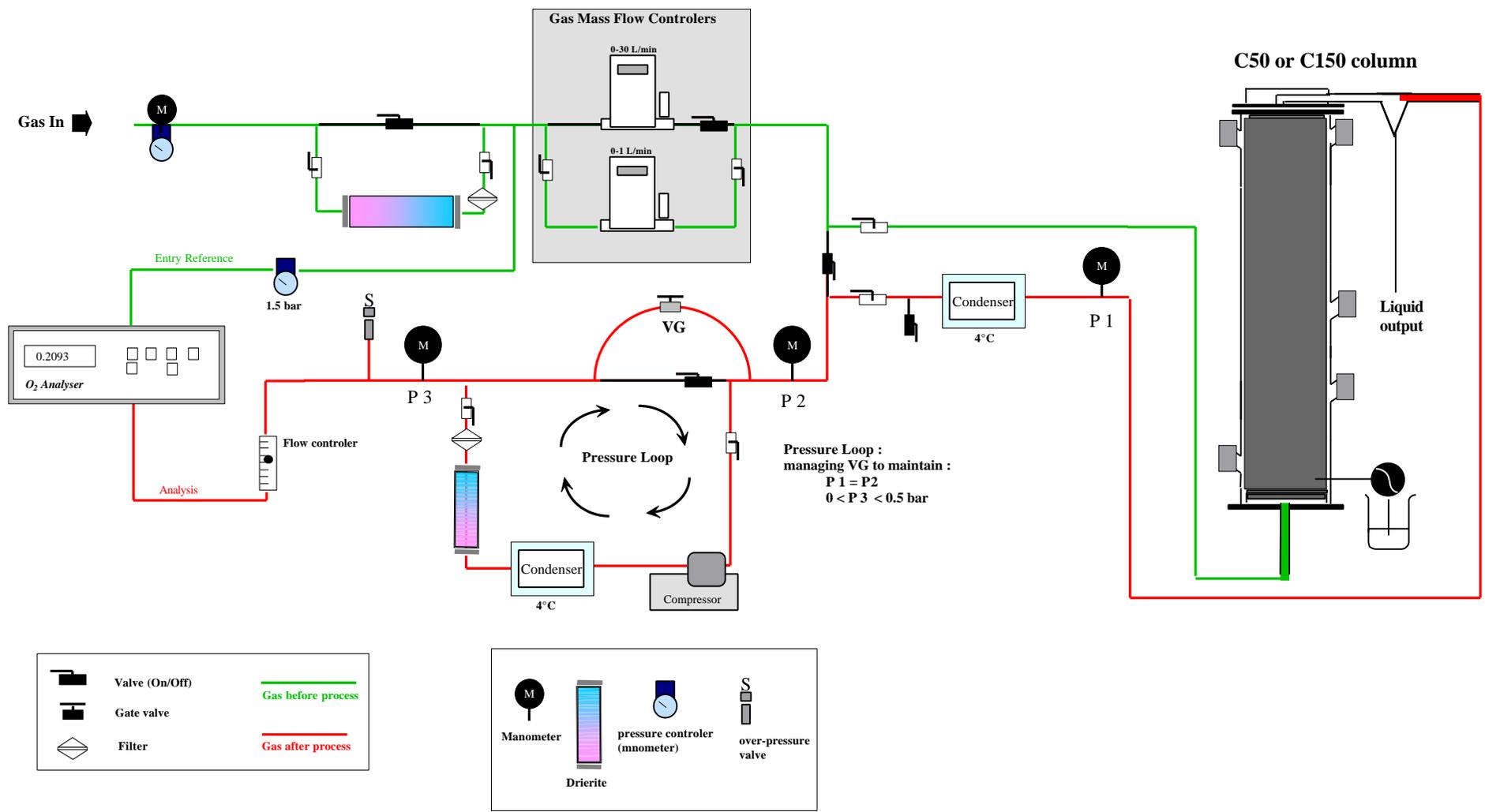
Figure 4 : Installation for C50 and C150 fixed bed columns experiments.

II.2 Gas and liquid loops and flow control

The representation of the installation for operating the columns is detailed in Figure 4. The installation serves as well for the C50 and the C150 column.

Air is used to feed the columns. It is dried before and after flowing through the columns. Pressure inside the column is currently assumed to be this measured by P1 manometer, installed at the output of the column. Even if two of the five points on the columns (one at the bottom and one at the top) can be used to measure the pressure drop, and then to have a better view of the pressure profile inside the column, the instrumentation is not presently ready for use. It can be noticed that for some KLa correlations (Table 5), the pressure drop is necessary. It also exists correlations for the calculation of pressure drop in fixed bed columns.

The pressure before the porous plate can be obtained with P2 manometer by manipulating the valves.

The pressure regulation loop has two objectives :
- First it avoids variation of the pressure for the gas analyser. This is important mainly for long time duration experiments (days).
- Secondly it can also be used to control the output pressure of the loop. The gas-balance method that we intend to develop for the KLa measurement (III.3) is sensitive to pressure inside the column.

Two gas mass flow controllers are used:
- 1 l.min^{-1} air (Aalborg GFC 17-07), for aeration of the C50 and C150 columns
- 0-30 l.min^{-1} air (Aalborg GFC 37-31), for aeration of the C150 column

The technical characteristics of the Aalborg gas flow controllers are given in Table 2.

Calibration	Standard condition (air , 1 atm, 21.1 °C)
Pressure	Max : 34.5 bar
	Optimal :1.4 bar
Repeatability	+/- 0.005 l.min^{-1}
Precision	+/- 0.015 l.min^{-1} (0.35 to 4.1 bar)
Temperature correction factors	0.0015 l.min^{-1} . °C^{-1}
Pressure correction factor	0.0015 l.min^{-1} . °bar^{-1}

Table 2 : Mass flow controllers technical characteristics.

The oxygen gas analyser used is an Oxymat 6E (Siemens). The main technical characteristics of the analyser are reported in table 3.

Standard measure range	15% - 21 % O_2
Repeatability	+/- 0.06% (for the range selected)
Precision	+/- 0.06% (for the range selected)
Signal variation	+/- 0.0375 % O_2
Stability (zero point and measure)	+/- 0.025 % O_2 / month
Measured gas	0.5 – 1.5 bar 18 – 60 $l.h^{-1}$ (0.3 – 1 $l.min^{-1}$)

Table 3 : Oxymat 6E technical characteristics.

It can be noticed in Table 3 that the minimum flow rate required by the analyser is 0.3 $l.min^{-1}$, then on the C50 column, with the gas flow controller 0-1 $l.min^{-1}$, only flow rates greater than 0.3 $l.min^{-1}$ would be used. Nevertheless, technical experience has shown that lower flow rates (0-0.3 L/min range) can be used but the response time of the analyser is higher mainly due to higher residence times in the internal tubing of the analyser.

III $\underline{K_L}$a measurement

One of the objectives of the LGCB columns is the study of the oxygen gas/liquid transfer inside a fixed bed for various operating conditions. The gas/liquid transfer is characterised by the volumetric transfer coefficient (K_La).
The techniques used for the K_La measurements with UAB columns were (TN 52.31):

- the sulphite method.
- the "gas in/ gas out" method using an oxygen dissolved electrode.

As previously mentioned, with the UAB nitrifying columns, the fixed bed is affected by the bottom and the top of the column. The columns built at LGCB are reduced to the fixed part only, therefore allowing a direct observation of the bed behaviour.

It can be also noticed that the classical sulphite method is not well adapted to a process involving liquid flow rate (continuous reactor), and that the method requires a long time for each measurement (at least 3 – 4 hours on the UAB bench columns). Also it must be noticed that the classical sulphite method, involving regular sampling of liquid and sulphite measurements versus time is not well adapted to a process involving liquid flow rate (continuous reactor). Such a method requires long time for obtainning representative decrease of sulphite concentration (corresponding to oxidation) leading to 3-4 hours for each measurements.

A **new method** for rapid KLa determination for processes with gas and liquid flows is then developed and presented here : a sulphite gas balanced method.

III.1 Sulphite gas balance method

III.1.1 Principle
The classical sulphite method (AFNOR X42-103) is based on measurements in the liquid phase and requires at least :
- to have an homogenous liquid phase;
- to follow a kinetic reaction of sulphite oxidation in the liquid;
- to have at least 10 sulphite concentrations measurement with a total variation of at least 0.15 mol/l having an estimation of O2 transfer rate with a reasonable accuracy.

The "sulphite gas balance" method developed at LGCB is based on this classical sulphite method, but instead of the measurement of the sulphite oxidation in the liquid phase, the difference of the oxygen fraction in the gas phase from the input (y^E) to the output (y^S)of the reactor (i.e. gas balance) is measured. The experimental protocol of the sulphite gas balance KLa measurement is detailed in figure 5.

The liquid phase in the reactor and the liquid feed if reactor operates in continuous, is a sulphite solution of 50g/l of Na₂SO₃. The sulphite reacts with the dissolved oxygen as follows:

$$SO_3^{2-} + \frac{1}{2}O_2 \xrightarrow{\quad k=f(co^{2+})\quad} 2\,SO_4^{2-}$$
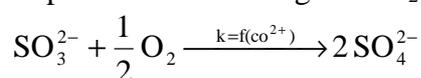
It must be outlined that the cobalt which catalyses the reaction can also accelerate the as/liquid transfer of oxygen if it is taken over 10^{-6} mol/l.

The kinetic law is complex, but under specific conditions, the kinetic rate can be considered as of zero order for the sulphite, 2nd order for the oxygen and first order for the cobalt (catalyst of the reaction). Then,

$$r_{O_2} = k\, C_{C_O 2+}\left[C_{O_2}\right]^2 = k'\left[C_{O_2}\right]^2$$

$$r_{SO_3^{2-}} = 2.r_{O_2}$$

$$r_{SO_4^{2-}} = -r_{O_2}$$

k depends on the temperature, on pH and on the ionic strength.. In principle if the sulphite concentration is maintained above 20 g/l the reaction is sufficiently rapid to instantaneously consumed all the oxygen transferred (C_{O2}#0 mol/l).

Then, as at any point of the reactor the dissolved oxygen concentration is zero, the knowledge of the hydrodynamic of the liquid phase is not necessary. On the other hand, as the method is based on the oxygen balance of the gas phase, the hydrodynamic of this phase must be known.

For a given reactor, operating conditions (namely gas and liquid flow rates) can be changed, and variation of the gas composition (y^S) can be followed online. The dynamic of the response depends on the gas residence time and on the design of the gas circuit (cleaning of the circuit) but is at steady-state after at most 10-15 minutes. The dynamic of the response itself can be used to study the dynamic of the system, but the lag due to the gas circuit must be known.
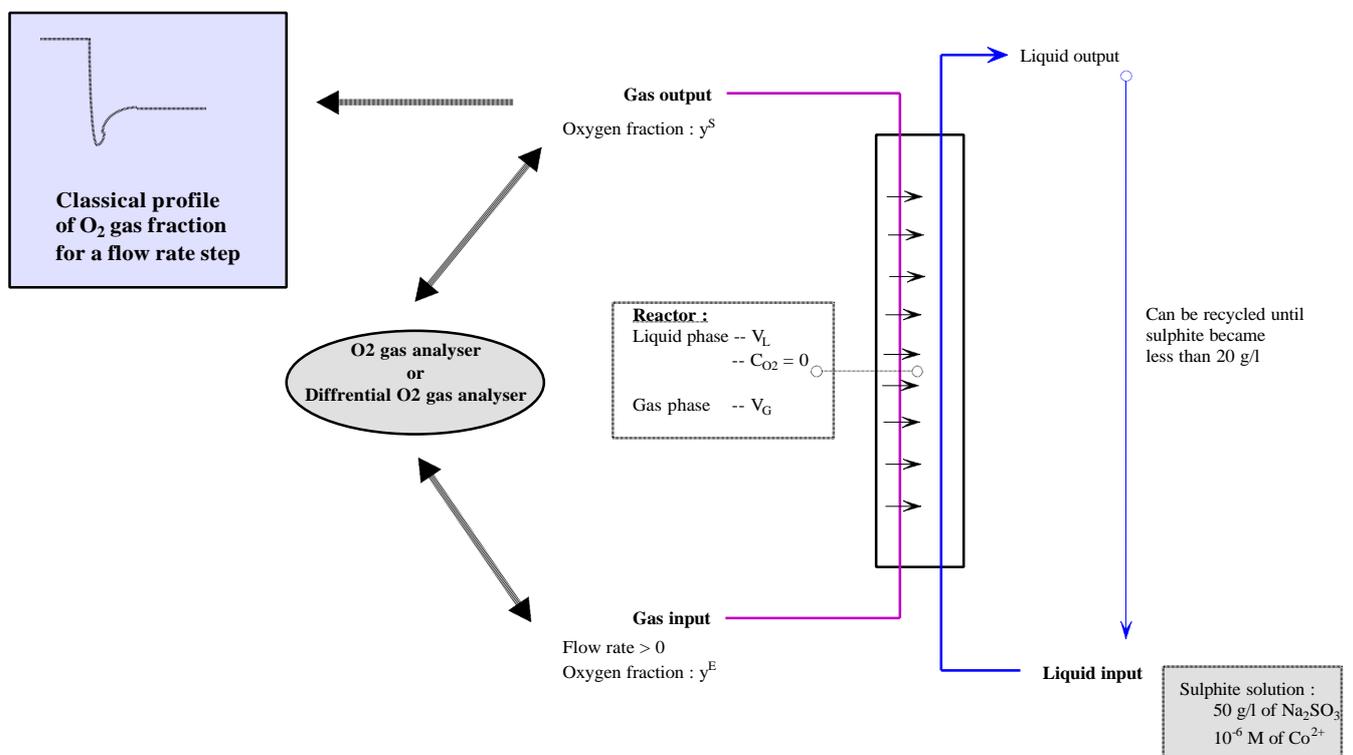

Figure 5 : Principle of the sulphite gas balance method for KLa measurement

III.1.2 $K_L a$ calculation

Two approaches can be used for the calculation of the KLa.

- The first is based on correlations established from analytical analysis of the steady-state mass balances for the mass transfer between phases. Usually, protocols such as NF-X-42-103, use correlation that can be simply applied. The correlation established for the sulphite gas balance method are presented here;

- The second is based on the identification of the $K_L a$ parameter. This approach required a parametric model (which is not necessary linear), and is used for problems without analytical or simple solutions. This approach will be used with the NitriSim model (SimLab toolbox) and is described in section III.3.

III.1.2.1 Relations for steady-state mass balance analysis of the mass transfer between gas and liquid phases
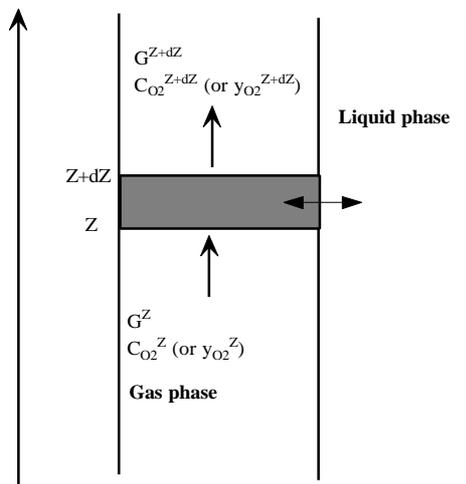
The gas phase is assumed to be plug flow

Whatever is the hydrodynamic of the liquid phase (from perfectly mixed to plug flow), the dissolved oxygen concentration is assumed to be zero.

Notations :

E : Acceleration factor of oxygen transfer. For some operating condition (high concentration of catalyst for example), the chemical reaction (here oxidation of sulphite) is sufficiently fast to modify the thickness (decrease) of the liquid film around the bubbles . This result in an observed transfer rate greater than the physical transfer.

K_L : mass transfer coefficient. For gases of low solubility (transfer resistance on the liquid size only), it can be assumed $K_L = k_L$

$K_L a$ ($k_L a$) :volumetric gas transfer coefficient (time^{-1})

$C_{O2}^{*-Z}\big|_{Liquid}$: saturation concentration of oxygen in liquid at z

$C_{O2}^{Z}\big|_{Gas}$: oxygen concentration in gas phase at z

G_Z : volumetric gas flow rate at z

G_Z^m : molar gas flow rate

Pz : total gas pressure at z

dV_{L-z} : Liquid volume between Z and Z+dZ

H : Henry constant

y^Z : gas fraction at Z.

Liquid phase oxygen balance:

plug flow	Perfectly mixed
$EK_L a.C_{O2}^{*-Z}\big|_{Liquid} + r_{O2}\big|_Z = 0$	$EK_L a.C_{O2}^{*}\big|_{Liquid} + r_{O2} = 0$

Gas phase oxygen balance:

For an element dZ :

$$G_Z.C_{O2}^Z\big|_{Gas} - G_{Z+dZ}.C_{O2}^{Z+dZ}\big|_{Gas} - EK_L a.C_{O2}^{*-Z}\big|_{Liquid}.dV_{L-Z} = 0$$

This can also be expressed as function of gas fraction by :

$$G_Z^m.y_{O2}^Z\big|_{Gas} - G_{Z+dZ}^m.y_{O2}^{Z+dZ}\big|_{Gas} - EK_L a.C_{O2}^{*-Z}\big|_{Liquid}.dV_{L-Z} = 0$$

with $G_Z^m = G_Z.\dfrac{P_Z}{RT}$

	Notes
Relation 1	
$E.K_L a = \dfrac{G}{V_L}\dfrac{y^E - y^S}{C*}$ $C* = \dfrac{P_e.Y^E - P_s.y^S}{H.\ln\left[\dfrac{P_e.Y^E}{P_s.Y^S}\right]}$	This relation is for constant molar gas flow rate, constant volume ; variable pressure **If Pe=Ps , this is equivalent to correlation 2.**
Relation 2	
$E.K_L a = \dfrac{G.H}{P.V_L}.\ln\left(\dfrac{y^E}{Y^S}\right)$	This relation is for constant molar gas flow rate, constant volume ; constant pressure
Relation 3	
$E.K_L a = \dfrac{\dfrac{1}{1-y^E} - \dfrac{1}{1-y^S} + \ln\left[\dfrac{y^E.(1-y^S)}{y^S.(1-y^E)}\right]}{\left(\dfrac{V_L.P}{G_0.H}\right)}$	This relation is for variable molar gas flow rate, constant volume ; constant pressure. Go : volumetric flow rate of inert gas (N_2)

III.1.2.2 Sulphite solution versus pure water.

It is important to kept in mind that sulphite solutions (i.e. sulphite method for K_La measurement), has some differences with the behaviour of pure water solution, mainly :

- There is a difference of viscosity for the two solutions. Moreover, the sulphite solution has a non-coalescent behaviour while water has a coalescent behaviour. If the impact on the $K_L a$ is negligeable with gas sparger giving "large buble", it may be important on gas distribution giving "small bubbles" (size of some microns).

- As previously remarked, sulphite can accelerate the gas transfer, for large amount of catalyst (10^{-4} M instead of 10^{-6} M). Catalyst is Mo^{2+} (AFNOR X42-103), but any kind of metallic bivalent cation (X^{2+}) can act as catalyst of the reaction.

- The saturation constant of oxygen in liquid phase (C_{O2}^*) is modified by the sulphite and sulphate ions. Then the constant use to calculate C_{O2}^*, i.e. Henry constant or partition coefficient, must be corrected taking into account the "salting out effect". This can be done using the Setchenov coefficient (Table 4-1) with the corresponding relation. Another model is also proposed by Shumpe (1993) (Table 4-2). It can be noticed that the evolution of the composition of the solution during oxidation of the sulphite to sulphate can affect the C_{O2}^*. With a solution of sulphite the C_{O2}^* at the beginning is 96.8% of the solution with sulphate, when sulphite was completely oxidised.

	Hi (l/mol)	+/-
H+	-0,2	0,003
Li+	-0,06	0,008
Na+	0	0,009
K+	-0,013	0,01
Rb+	-0,025	0,005
Cs+	-0,041	0,011
NH4+	-0,098	0,005
Mg2+	-0,025	0,002
Ca2+	-0,015	0,001
Ba2+	0,003	0,001
Mn2+	-0,029	0,006
Co2+	-0,021	0,005
Ni2+	-0,022	0,004
Cu2+	-0,03	0,007
Zn2+	-0,024	0,004
Cd2+	-0,031	0,004
Al3+	-0,018	0,001
Fe3+	-0,032	0,005
La3+	-0,014	0,004
Ce3+	-0,015	0,007
Th4+	-0,017	0
Cl-	0,257	0,009
NO3-	0,22	0,01
OH-	0,34	0,006
HSO42-	0,33	0,004
SO42-	0,163	0,006

$$\log\left(\frac{H°}{H}\right) = \log\left(\frac{k°}{k}\right) = k_{sc}.Cs$$

$$k_{sc} = \frac{1}{2}\sum_i H_i x_i z_i^2 \quad \text{(Setchenov coefficient)}$$

k = partition coefficient
H = Henry constant
Xi = molar liquid fraction of ion i
Zi = electric charge of ion i
Cs = solution concentration

Reference : Werner Lang and Rolf Zander. Salting out of oxygen from aqueous Electrolyte solution : Prediction and mesurement Ind. Eng. Chem Fundam. 1986. 25.N°4. 775-782

Table 4-1 : Setchenov coefficient for the correction of the Salting out effect.

Salt	hi (l/mol)	Salt	hi (l/mol)	Gas	hG (l/mol)
H+	0	HO-	0,0769	O2	0
Li+	0,0691	F-	0,1016	CO2	-0,0183
Na+	0,1171	Cl-	0,0334	N2O	-0,011
K+	0,0959	Br-	0,0137	C2H2	-0,0174
Rb+	0,0845	J-	0,002	C2H4	0,0014
Cs+	0,066	NO3-	0,005	He	-0,036
NH4+	0,0539	ClO4-	0,0502	Ne	-0,02
Mg2+	0,1765	JO4-	0,1514	Ar	-0,009
Ca2+	0,1771	HCO3-	0,1372	Kr	0,003
Ba2+	0,2021	HSO3-	0,0543	Xe	0,005
Fe2+	0,1712	H2PO4-	0,1025	Rn	0,015
Co2+	0,1983	XO-	0,0765	H2	-0,024
Ni2+	0,2039	XOCH2COO-	-0,0119	N2O	-0,008
Cu2+	0,181	S2O3 --	0,1109	NO	0,004
Mn2+	0,162	HPO4 --	0,1789	C2H6	0,011
Zn2+	0,1712	CO3 --	0,1666		
Cd2+	0,2201	SO3 --	0,1537		
Al3+	0,2253	SO4 --	0,1185		
Fe3+	0,0996	PO4 ---	0,2117		
Cr3+	0,0595				

$$\log\left(\frac{C_G{}^\circ}{C_G}\right) = \sum (h_i + h_G).Ci$$

C_G = gas dissolved saturation concentration in solution
$C_G{}^\circ$ = gas dissolved saturation concentration in pure water (298.15°C)
h_G = gas constant
hi = salt constant
Ci = salt concentration

Reference : Shumpe A. The estimation of gas solubilities in salts solutions.
Chem Eng. Science. 48. 1. 153-158, 1993

<u>Table 4-2 :</u> Setchenov coefficient for the correction of the Salting out effect.

<u>III.2 Residence Time Distribution analysis</u>
As noted in introduction, hydrodynamic description of the fixed bed is one of the two problems encountered in the nitrifying columns modelling.
The LGCB column would be used to study hydrodynamic (RTD) of fixed bed and to analyse and identify the parameters involved. If these studies have not starting yet, they are planned and both NitriSim model and method that we intend to use for RTD studies have been discussed.

III.2.1 RTD and Hydrodynamic behaviour of the fixed bed and nitrifying columns

RTD experiments on UAB pilot and bench columns have shown that the overall behaviour of the nitrifying columns becomes the behaviour of a perfectly mixed reactor when liquid recycling flow rate and gas flow rate are increased.

But the liquid behaviour of the fixed bed itself is masked by the bottom and the top of the column (representing more than half of the liquid volume of the column for the bench nitrifying columns). This can be illustrated with the previous experiments performed by UAB. The RTD experiment 4 (Perez et al. TN 37.510) is performed without liquid recycling and with a low gas flow rate (40 ml/min). Tracer is injected at the bottom of the fixed bed, avoiding the mixing effect of the bottom of the column. In figure 6 are superposed the experimental RTD measured and the theoretical RTD for the fixed bed (as calculated at the output of the fixed bed part) and the theoretical RTD for the column (including top volume of the column). In Figure 6, peaks were identified, corresponding respectively to the fixed bed (i.e. part B) and the column (i.e. part B and C). The RTD measured is a mixing of the two RTD. The discrepancies in the end of the RTD are probably representative of a non perfect mixing (stagnant zones with retention of the tracer) (Berg et al., 1996).

Then, in anticipation of possible complex flow behaviours, several additions were implemented in the classical N-tank in series model (report to II.4.1).
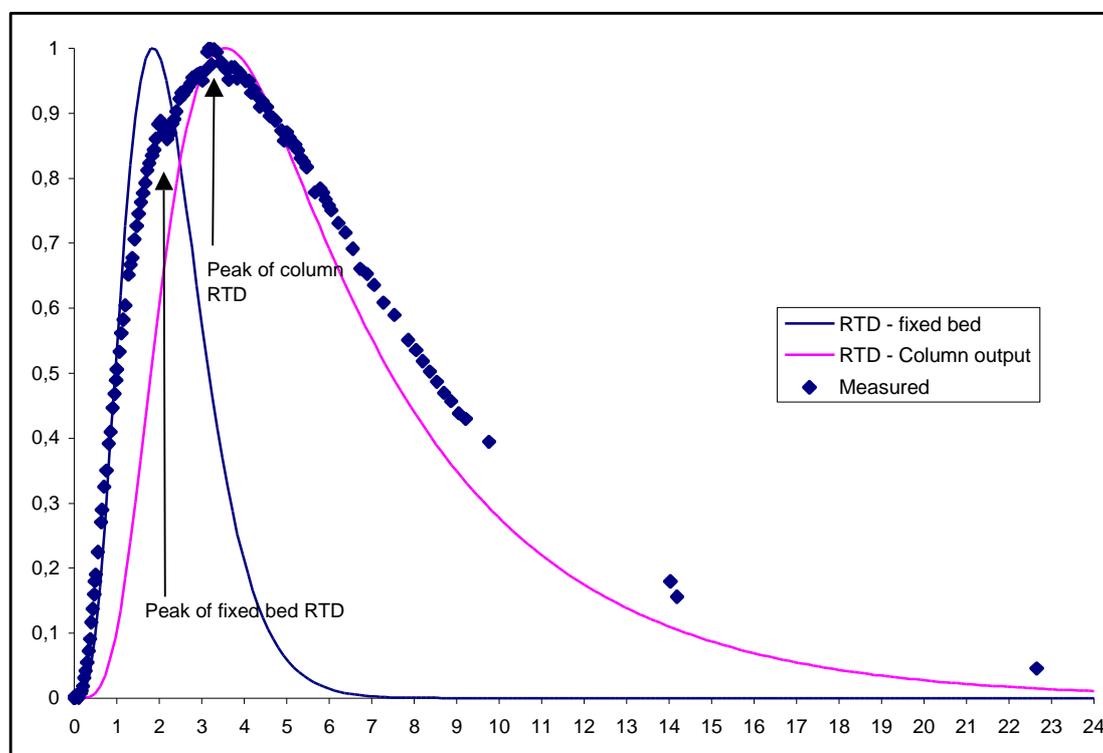

Figure 6: Measured and simulated (5-tanks in serie model without back-mixing) RTD for UAB bench column. Experiment 4 (liquid flow rate : 0.83ml/min; Gas flow rate 40 ml/min). All values were normalised to 1.

III.2.2 RTD measurement at LGCB

At the present time a conductimetric method is envisaged for RTD analysis on C50 and C150 columns.

This method is interesting because it afford a continuous online analysis for the RTD and will reduce manual operations (sampling, measurements). It is also possible to adapt this method for nitrifying operating columns (or other reactors).

The protocol reamains to be established.

It must be outlined that **the sulphite gas balance method is not sensitive to the hydrodynamic of the liquid phase**, because $C_{O2} = 0$ in all point of the liquid phase, except in liquid boundary interfaces surrounding air bubbles where the chemical reaction takes place.

III.3 NitriSim model modifications (SimLab version) : Columns dynamic model and parameter identification

III.3.1 Hydrodynamic model

The hydrodynamic model developed for the nitrifying columns, N-tanks in series with back-mixing between tanks, is used (TN 27.1, 27.2, 27.3, 39.2). The model was adapted to the Matlab© toolbox called SimLab, developed for studying laboratory scale biological and chemical processes. Several other options were added to the previous N-tanks model in order to cover a larger range of possible hydrodynamics (Figure 7).
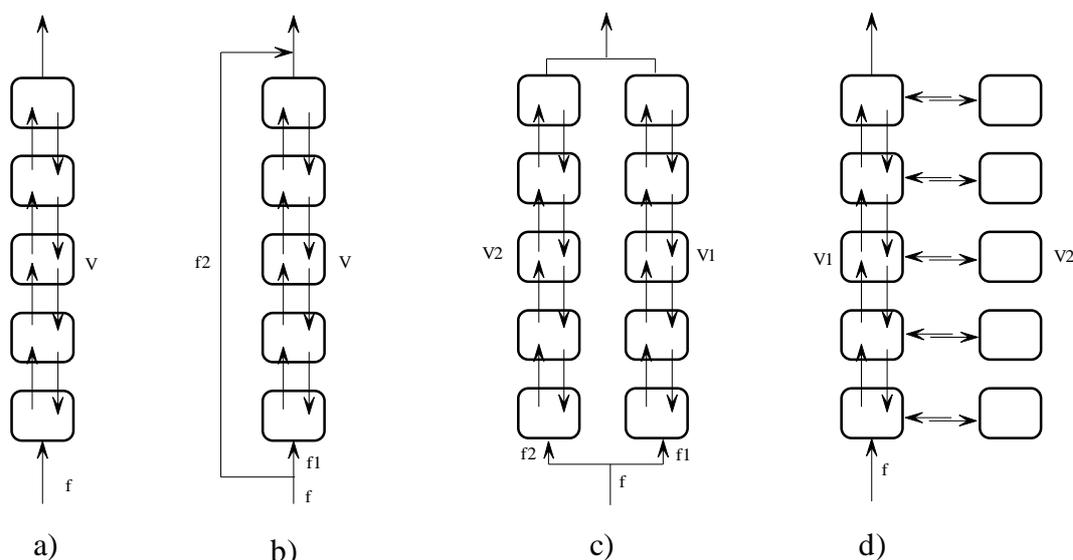
Figure 7 : Flow models available on the Simlab toolbox for fixed bed reactors. f, f1, f2 are flow rates (f=f1+f2) ; V, V1, V2 are volumes (V=V1+V2)
a) N-tank in series with back-mixing
b) N-tank in series with back-mixing and by-pass
c) N-tank in series with back-mixing and channelling in the bed
d) N-tank in series with back-mixing and dead volume (with or without exchange with the dynamic flow)

It may be important to keep in mind several aspects of the N-tanks in series model for the nitrifying columns.

- The mathematical griding of the columns into N-tanks is to be applied for all the 3 phases (solid , liquid , gas). This means that assuming the column is equivalent to 1 tank (i.e. perfectly mixed reactor model) implies also that <u>the fixed biomass is uniformly distributed</u> in the bed.

- The back-mixing is a way to represent the axial dispersion with N-tank in series models for defined in plug-flow behaviour. But it is rather here a way for reaching a perfect mixed behaviour for the liquid or the gas phase whatever is the number of tanks, keeping a non-uniform repartition of biomass into the bed.

III.3.2 Flow rates, volumes and pressure corrections

The NitriSim model intends to be flexible enough to represent any kind of operating situation. It has been observed that pressure drop can exist on fixed bed and that gas composition can change significantly.

To take into account the pressure drop (more generally pressure variation between bottom and top of the column) in the N-tanks in series model, it was assumed :
- That the pressure variation is uniformly distributed along the height of the column.
- That the pressure variation is compensated by a gas volume variation and not by a gas molar composition variation (i.e. ideal gas relation : PV=nRT), and that the overall gas volume of the column (measured by gas hold-up) is constant.

Then :

$$P_z = P_{bottom} + z.\frac{\Delta P}{L}$$

$$V_{G-z} = \frac{P_{bottom} V_{G-bottom}}{P_z} . \frac{V_{Tank-bottom}}{V_{Tank-z}} \qquad \text{and} \qquad \sum_z V_{G-z} = V_G$$

For $K_L a$ experiments, oxygen is transferred from the gas to the liquid. As a consequence the number of moles in the gas phase decreases. This affect necessary the gas molar flow rate (decrease the flow rate). If this effect can be neglected for small gas transfer, it must be taken into account for important change in the gas composition. The correlation 3 previously established takes into account this effect. Modification were also performed in the NitriSim model to take into account the variation of the gas composition. A factor is associated to the gas flow rate :

$$fG = \frac{n\_inert + \sum n\_i}{n\_input}$$

n_inert : moles of inert compounds in gas phase (no transfer with the gas phase)

n_i : moles of compound i in the gas phase in tank N

n_input : moles at the input of the column

III.3.3 Numerical solver for Ordinary Differential Equations integration and parameters identification

Matlab is an intuitive language and a technical computing environment. It provides core mathematics and advanced graphical tools for data analysis, visualisation and algorithm and application development. Matlab can be associated to companion toolboxes developed for specific applications (signal and image processing ; Data analysis ; Financial and economics analysis ; control systems design….).

As this language is used within the MELiSSA team as well by ADERSA for the development of algorithms for the processes control and UAB for modelling and identification, it was decided to develops also at LGCB models and applications with this language in order to facilitate exchanges in the MELiSSA team.

A Matlab toolbox for laboratory scale chemical and biological processing was initiated at LGCB. The toolbox called SimLab solves processes involving several reactions (chemical/biological), gas/liquid equilibria and acid/base equilibria for various hydrodynamic behaviour. The hydrodynamic model developed for the nitrifying columns (N-tanks in series), including the options detailed in section II.4.1, was integrated in the SimLab toolbox, and the parameters can be given through a user-friendly interface (Figure 8).

Figure 8 : interface of the SimLab toolbox for the N-tanks in series model of the nitrifying columns.

As detailed in TN 27.1,27.2, 27.3 an 39.2, the model for the nitrifying column is a set of n ordinary differential equations (ODE) for each phase (liquid, gas, solid) of the form :

$$\frac{dx_j}{dt} = f(x_{i(i=1,n)}, t) \text{ for each } x_j \text{ of the n compound}$$

The system of 3n ODE, is solved with the ODE toolboxes of Matlab. ODE15S, a variable order method, was chosen, being able to solve stiff and non stiff differential equations, and being also able to detect and solve Differential Algebraic Equation.

For parameters identification, a Gauss-Newton algorithm was developed in the Matlab language and integrated in the SimLab toolbox. The scripts developed for parameter identification have been designed in order to make the identification procedure easily manageable and to enable identification of any kind of parameter (hydrodynamic, kinetic, physical parameters). The principle of the procedure is presented in figure 9.
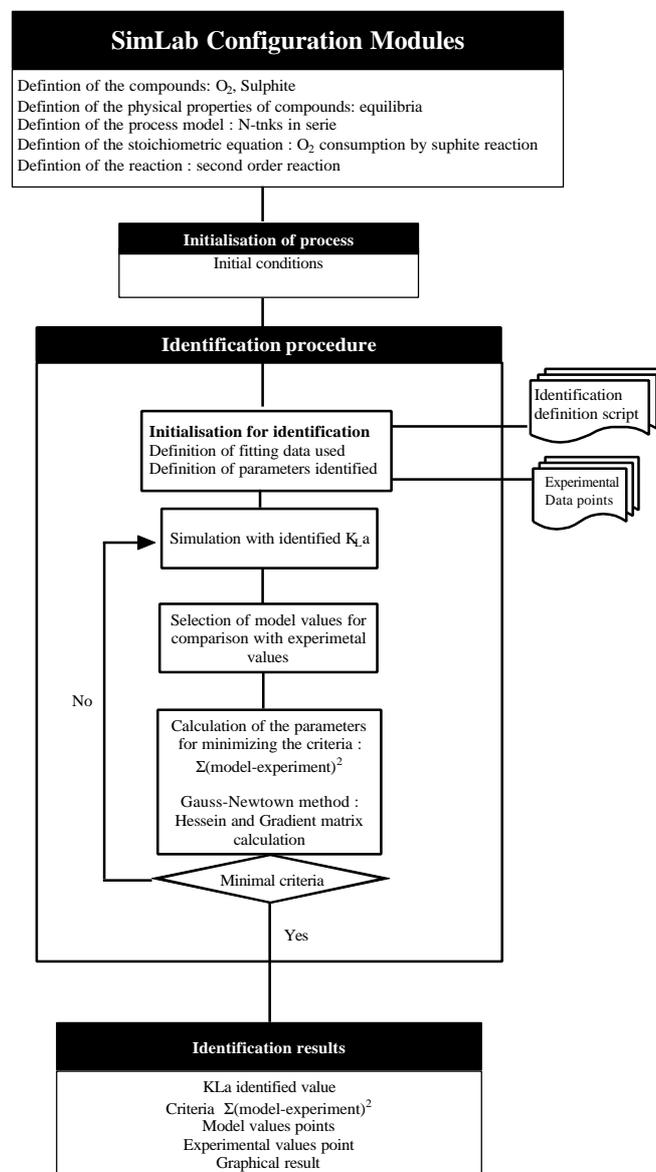

Figure 9 : Overview of identification procedure

IV Review of literature correlation for $K_L a$ in fixed bed columns

Mass transfer in fixed bed reactor is a process engineering problem which have been already studied. Fixed bed processes are often used in chemical engineering (lesser in biological processes engineering), and correlation have been established for the mass transfer in biphasic (gas/liquid) fixed bed columns.

Nevertheless, as can be seen in the Table 5, these correlations are dependant on the design of columns and of operating conditions. Parameters of these correlations must be adapted to the column and operating conditions used.

Correlation	Operating condition Columns design	References
Deront		
$k_L a = 1.69 . 10^{-4} \left(u_L \dfrac{dP}{dZ} \right)^{0.383}$	$1.15 . 10^{-3} < u_L < 2.69 . 10^{-3} \, m/s$ $1.28 . 10^{-3} < u_G < 3.85 . 10^{-3} \, m/s$ Biolite beads of 2.7 mm diameter Fixed bed of 0.5x3.3 to 0.5x4.6 m Nitrfying column	Deront M., Samb F.M., Adler N. and Peringer P. (1998) Volumetric oxygen mass transfer coefficient in an upflow cocurrent packed-bed Bioreactor. Chemical Eng. Science. 53, 7, 1321-1330
Saada		
$Sh = a . Re_G^b . Re_L^c . \left(\dfrac{Dc}{dp} \right)^d$ $k_L a = \dfrac{Sh . D_A}{dp^2}$ Dc : column diameter Dp : particle diameter D_A : air diffusion in water ReL and ReG are respectively the Reynolds fo Liquid and Gas	$0.17 \le G \le 7 \; kg/m^2 . s$ $8 \le L \le 100 \; kg/m^2 . s$ $0.51 \le dp \le 2.14 \; mm$ a=10.72 b=0.22 biphasic in pores c=-0.32	Saada M.Y. (1975) Fluid mechanics of co-current two phase flow in packed beds : pressure drop and liquid holdup studies. Per. Poly. Chem.Eng. 19. 317-337
Alexander		
$k_L a = a . L^b . G^c$	$0.002 \le G \le 0.04 \; kg/m^2 . s$ $0.9 \le L \le 6 \; kg/m^2 . s$ $3.17 \le dp \le 12.7 \; mm$ a=0.181 b=0.4 for beads c=-0.644	Alexander B.F. and Shah Y.T. (1976) Gas-Liquid mass transfer coefficients for co-current upflow in packed beds – effect of packing shape at low flow rates. Can. J. Chem. Eng. 54. 556-559.
Marquez		
$k_L a = 1.026 . dp^{-0.51} u_L^{-0.51} . u_G^{0.42}$	$0.01 \le G \le 0.2 \; kg/m^2 . s$ $5 \le L \le 32 \; kg/m^2 . s$ $1 \le dp \le 3 \; mm$	Marquez A.L. (1992) Les réacteur à lit fixe à co-courant vers le haut de gaz et de liquide. Etude du transfer de matière gaz-liquide . Thèse INPL.

Table 5 : Literature correlation for $K_L a$ in co-current flow fixed bed

In the correlation of Saada (1975), the Reynolds of Gas and Liquid are involved. For the liquid phase, this suppose to know the viscosity of the liquid phase. It must be kept in mind that we have used the viscosity of water for calculations instead of the viscosity of a sulphite solution.

In the correlation of Deront et al. (1998), pressure drop measurement is required. As previously said, the pressure drop inside the LGCB column is not currently measured, then this parameter not known. It can be found several correlation for the prediction of pressure drop inside column, which, as the correlation for the K_La largely depends on the columns design and operating conditions.

For the correlation of Deront et al. (1998), the pressure drop correlation proposed by Barios et al. (1987) was chosen. The parameters of the model that we used are those for bubbles.

$$\frac{(\Delta P_{GL})_t}{Z} = \left[A \left(\frac{\Delta P_L}{Z} u_L \right)^B + C \left(\frac{\Delta P_G}{Z} u_G \right)^D + g.(L.\boldsymbol{b}_L + G.\boldsymbol{b}_G) \right] \left(\frac{E}{u_L + u_G} \right) \text{ (in Pa.m}^{-1})$$

	A	B	C	D	E
Bubbles	**1,5**	**1**	**108,7**	**0,395**	**4,64**
Pulse	13,8	1	5	0,935	1
Fog	875,6	0,735	1,6	0,935	1

V Experiments and results

The first phase of experiments where performed with the column C50. These first experiments are used to check the column configuration and the "sulphite gas balance" method for K_La measurement.

V.1 Final design of the C50 column

The characteristics of the C50 column in fixed bed configuration is detailed in the following Table 6. The hold-up, and the correlation established and presented in table 6, are measured for different gas flow rate, but without liquid circulation (see to Figure 1). These characteristic were used for simulation (NitriSim) and with K_La relations

Column C50

Height : 1.015m
Diameter : 53 mm
Total volume : 2.26 L
Section : 20.21 10^{-4} m^2

Glass beads diameter : 4mm

Characteristic dimensions :
D/d : 13.25
Voidage measured (with beads) : 0.35

Liquid flows:
Flows rates : 0 –10 L/h
RT : 0.07 h – inf

Gas flows :
Flows rates : 0.05 – 1 L/min
Vo max : 0.0249 m/s

Hold-up :
H=0.0033*G-2.10^{-5} G^2
        H : hold up in liter
        G : Gas flow rate in l/min

Table 6 : Characteristic and operations of fixed bed C50 column

V.2 Preliminary observations with the **bubble column configuration**

The first set of experiments were performed for a **"bubble" column configuration** (i.e. the beads were not introduced in the C50 column). This configuration is easiest to manage than a fixed bed configuration and is then useful for testing and checking :

- The sulphite gas balance protocol
- The coalescence and the distribution of bubbles
- The effect of the gas sparger.

V.2.1 General remarks for the sulphite gas balance method

First comments on the calculation of K_La measured by the sulphite gas balance method can be found in section IV.1.3.

The sulphite gas balance method works well, but several precaution must be taken :

- It is necessary to check the composition of the gas at the input, using the same circuit as for the gas output composition measurement, but short circuiting the column. As can be seen in the expression of the correlations for KLa calculation, the method is based on the differential analysis of input and output and is very sensitive to bad measurement of input composition, especially for small K_La values.
- The precision of Oxymat 6E (Table 3) do not allow the application of the method for low K_La (i.e. variation of the composition below the sensitivity of the analyser).
- The calculations are sensitive to the pressure inside the column which must be controlled.

V.2.2 Pure water and sulphite solution : the effect of coalescence

The effect of coalescence of bubble with pure water was not measured but was observed in the column. As will be discussed below the bubbles formed by the porous plate are very small, inducing then a higher K_La, but in water the bubbles coalesce (while not in sulphite solution).

Influence can be measured using another method than sulphite based method for K_La measurement, such as an electrode method or by the reduction of non-coalescence effect by addition of compound reducing surface tension of the solution in sulphite solution.

It is important to keep in mind that in principle nitrifying columns operate in coalescent solution.

V.2.3 Gas sparger and porous plate : the effect of gas dispersion and of bubble size

It was observed that the porous plate generates very small bubbles. The "bubble" column configuration was then used to study the effect of the gas distribution system on the value of K_La.

Three experiments were then compared : one with the porous plate and one with a more classical gas sparger based on a 0.5 mm needle (Figure 10). The experiments were performed for a gas flow rate of 1L.min^{-1} (0.45 VVM) and no liquid flow rate. Results are reported in Table 6

Porous plate   **0.5 mm needle**   **Direct gas feeding**
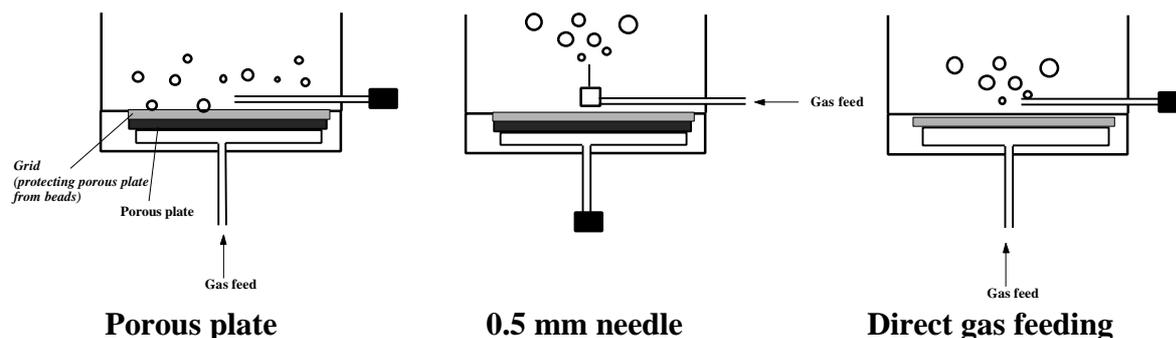
<u>Figure 10 :</u> Testing 2 gas distribution system

	Relation 1	**Relation 2**	**Relation 3**	**NitriSim 1**	**NitriSim 2**
Porous plate	96	96	119	99	117
0.5 mm needle	38	38	48	39	47
Direct gas feeding	16	16	21	17	20

<u>Table 6 :</u> Comparison of K_La (h^{-1}) calculated by sulphite gas balance method for a gas flow rate of 1 l.min^{-1} (0.45 VVM) in C50 "bubble column" NitriSim 1 is the value identified with NitriSim, 10 tanks in series without back-mixing and without correction on gas flow rate, while NitriSim 2 include correction on gas flow rate. As no pressure drop are considered, relations 1 and 2 gives the same result.

First it can be noticed that the effect of the variation of the composition of the gas phase is not negligible on the calculation of the K_La. The correlation with and without this correction present a difference of 20% both with the porous plate and the needle system.

The K_La identification with NitriSim models (respectively 1 and 2), for 10 tanks in series and no back-mixing, give consistent values compared to the correlations (respectively 1-2 and 3).

The effect of the gas distribution system is important and is visible because of the non coalescent behaviour of the sulphite solution. With the porous plate, the K_La is about 2.5 time higher than with the needle in the bubble column and 6 times higher than with a direct gas feeding. The effect would be lesser with fixed bed column because of the effect of coalescence and breaking of bubbles between beds.

It would be interesting to observe the effect of the gas distribution system with a coalescent solution (pure water).

<u>V.3 K_La measurement in C50 fixed bed column</u>

The C50 column was used to validate and define the protocol for the K_La measurement from the sulphite gas balance method.

Some previous results obtained on bench columns, which diameter is closed to the C50 diameter are presented in Table 7. It can be seen that superficial gas velocities in UAB bench

column are in the lowest range (about 0.05 L/min) of the mass flow controller used for the C50 gas feed, and then above the lowest limit of the O_2 analyser.

We have focused the studies on the reliability of the K_La values measured with the sulphite gas balance method.

The results are presented in Table 8b. The liquid flow rate is higher than in UAB bench column, and the gas flow rate covers the 0.05-1l/min range (Table 8a).

Experiment	voidage	$V°_G$ (m/s)	$V°_L$ (M/s)	Kla (h^{-1})
M1	0,55	$5,49.10^{-4}$	$1,32.10^{-4}$	67
M2	0,55	$1,37.10^{-3}$	$1,32.10^{-4}$	56
M3	0,55	$1,24.10^{-4}$	$1,32.10^{-4}$	23
M4	0,55	$1,24.10^{-4}$	$1,32.10^{-4}$	34
M5	0,55	$2,06.10^{-4}$	$1,32.10^{-4}$	24
M6	0,55	$5,49.10^{-4}$	$1,32.10^{-4}$	36

Table 7 : Previous results - K_La identified on UAB bench column from nitrifying experiments. M1-M6 are UAB experiments as detailed in TN 39.2. All values are for the fixed bed part.

V.3.1 Analysis of the stability of the y^S measurement

The gas method used is developed as a rapid method for K_La measurement. Whatever is the process with which this method is used, it is necessary to know if the measurement is stable. The sulphite gas balance method developed here (i.e. the relations presented in section III.1.2.1) can only be used for a steady state process. This supposes also that the gas fraction at the output is also in steady-state. A non steady-state gas fraction, what is the result of a non steady state process, will lead to problem in repeatability of K_La measurement.

Therefore, experiments for the analysis of the steady-state of the oxygen gas fraction at the output of the column have been be performed. This was done by measuring the gas fraction until complete oxidation of sulphite in an experiment with a closed loop for liquid between output and input. Three tests were performed, called "test exhaustion 1; 2; 3". The range of variation for K_La obtained are reported in Figure 11.

Experiment 1 was performed with an initial sulphite concentration of 50g/l.

Experiment 2, with an initial sulphite concentration of 10g/l was repeated two times.

The results of experiment 3 are reported in Figure 10.

On this 3 hours experiments, it can be observed that the gas fraction tends to increase with time (Figure 10 [1]). During the experiment, by "shaking" [2] the column, it seems that that some bubbles locked in the column are released what reduce the gas fraction and stop temporally the increase observed. On this experiments, the K_LA variations are of 11%, what is higher than the 3% that would be due to the variation of oxygen saturation concentration with the variation of the composition of the solution (oxidation of sulphite to sulphate). It must be outlined that for given operating conditions (given flow rates, fixed volumes), the increase of gas fraction at the output results in a decrease of the K_La. Considering the evolution of the oxygen gas fraction, K_La measured will be higher at the beginning of experiments.

The comparison of these experiments seems indicate that sulphite concentration plays a non negligible role. As the changes in the dissolved oxygen saturation concentration with sulphite concentrations are taken into account in $K_L a$ calculations, if initial concentration of sulphite play a role, this may be a role on the hydrodynamics of the columns. This is perhaps related to the viscosity or/and the coalescence of the sulphite solution, which affect the behaviour of bubbles in the column.

The evolution of the gas fraction is probably due to variations in volumes inside the column (gas and liquid volume) during the experiments. As shacking the column affects the column it is possible that some bubbles remains prisoners in the bed (creating gas dead volumes).

Sulphite solutions with lower initial concentration (i.e. 10 g/l) are "more" comparable to water (i.e. biological condition), and variation observed in the $K_L a$ measured are lower.

It would be useful to perform the stability experiment for a longer period to check if and when the steady-state is reached.

This analysis of stability outline a critical parameter for the sulphite gas balance method : the volume (liquid or gas, as they are linked) which must be accurately measured. Related to the gas phase, the pressure is also important to take into account.
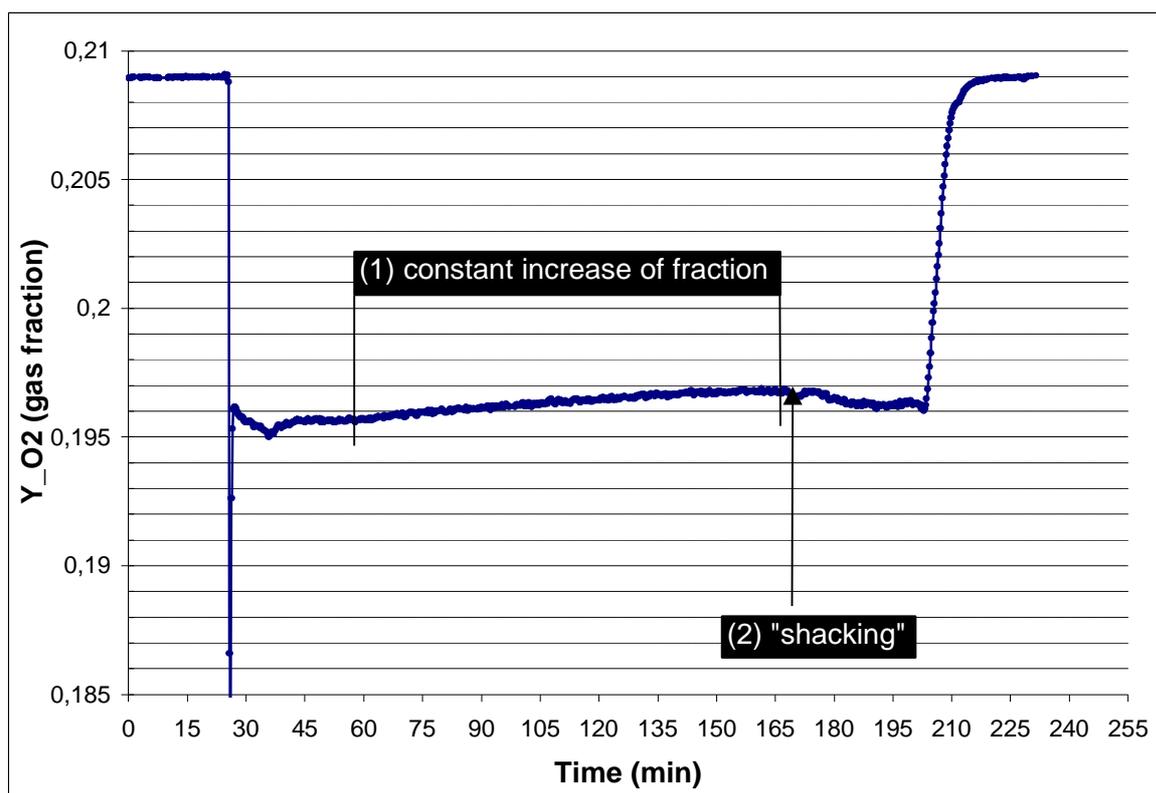

Figure 10 : Analysis of the stability of the y^S (O_2 output gas fraction) measured. Experiment on C50 fixed bed column. Gas flow rate : 1l/min ; Liquid flow rate 2l/h (looped liquid circuit); Na_2SO_3 initial concentration : 50 g/l.

V.3.2 K_La measurement on C50 column

Several series of experiments were performed for the measurement of K_La. A series correspond to online measurement of gas fraction with the same liquid, recycled until end of the series or complete exhaustion of sulphite, by increasing or decreasing the gas flow rate. Two series are presented here. Details are reported in Table 8a. The K_La values calculated and identified are reported in Table 8b.

Because of the variation of the gas fraction (as discussed above), a series with increasing gas flow rate (S6), and one with reducing gas flow rate (S7) are complementary. **In order to reduce K_La variation (gas fraction variation) sulphite solution of 10g/L were used**.

As can be seen in Figure 11, only K_La measured for limits of the range of flow rates are different (i.e. 0.3 L/min and 1 L/min). Medium K_La values (i.e. between 0.5-0.8 L/min) are comparable in the series, the column having run during the same period when the gas fraction was measured.

Experiment	G (L.min)	F (L.min)	VG (m/s)	VF (m/s)	Gas flow changes
S7-1	1	2,074	2,16E-02	7,46E-04	Start of series
S7-1	1	2,074	2,16E-02	7,46E-04	By decreasing
S7-0.9	0,9	2,074	1,94E-02	7,46E-04	By decreasing
S7-0.8	0,8	2,074	1,73E-02	7,46E-04	By decreasing
S7-0.7	0,7	2,074	1,51E-02	7,46E-04	By decreasing
S7-0.6	0,6	2,074	1,30E-02	7,46E-04	By decreasing
S7-0.5	0,5	2,074	1,08E-02	7,46E-04	By decreasing
S7-0.4	0,4	2,074	8,63E-03	7,46E-04	By decreasing
S7-0.3	0,3	2,074	6,48E-03	7,46E-04	By decreasing
S7-0.2	0,2	2,074	4,32E-03	7,46E-04	By decreasing
S7-0.1	0,1	2,074	2,16E-03	7,46E-04	By decreasing
S7-0.05	0,05	2,074	1,08E-03	7,46E-04	By decreasing
S6-1	1	2,074	2,16E-02	7,46E-04	By increase
S6-0.9	0,9	2,074	1,94E-02	7,46E-04	By increase
S6-0.8	0,8	2,074	1,73E-02	7,46E-04	By increase
S6-0.7	0,7	2,074	1,51E-02	7,46E-04	By increase
S6-0.6	0,6	2,074	1,30E-02	7,46E-04	By increase
S6-0.5	0,5	2,074	1,08E-02	7,46E-04	By increase
S6-0.4	0,4	2,074	8,63E-03	7,46E-04	By increase
S6-0.3	0,3	2,074	6,48E-03	7,46E-04	Start of series

Table 8a : Experimental operating conditions on C50 column

Experiment	R1	R3	NitriSim 1	NitriSim 2	C1	C2	C3	C4
S7-1	209,13	259,64	-	-	1,8	2,08	2,19	18,89
S7-1	203,36	252,63	-	-	1,8	2,08	2,19	18,89
S7-0.9	196,46	243,78	-	-	1,81	2,04	2,34	18,07
S7-0.8	182,62	226,44	-	-	1,83	1,98	2,53	17,20
S7-0.7	166,92	206,84	-	-	1,85	1,93	2,75	16,26
S7-0.6	150,49	186,29	-	-	1,87	1,86	3,04	15,24
S7-0.5	133,40	164,95	-	-	1,9	1,79	3,42	14,12
S7-0.4	114,51	141,32	-	-	1,93	1,7	3,95	12,86
S7-0.3	93,75	115,40	-	-	1,97	1,6	4,75	11,39
S7-0.2	69,98	85,84	-	-	2,04	1,46	6,17	9,61
S7-0.1	44,90	54,60	-	-	2,14	1,26	9,65	7,18
S7-0.05	24,10	30,14	-	-	2,21	1,08	15,07	5,37
S6-1	192,16	238,91	197.61	236.10	1,8	2,08	2,19	18,89
S6-0.9	184,77	229,48	183.18	219.80	1,81	2,04	2,34	18,07
S6-0.8	175,83	218,13	171.63	204.61	1,83	1,98	2,53	17,20
S6-0.7	166,37	206,13	155.74	186.23	1,85	1,93	2,75	16,26
S6-0.6	150,88	186,73	138.74	165.38	1,87	1,86	3,04	15,24
S6-0.5	134,09	165,67	123.35	147.03	1,9	1,79	3,42	14,12
S6-0.4	120,39	148,32	109.65	129.07	1,93	1,7	3,95	12,86
S6-0.3	106,25	130,35	91.98	109.02	1,97	1,6	4,75	11,39

Table 8b : K_La measured by sulphite gas balance method using relations 1 [R1] and 2 [R2] ; using identification procedure with dynamic models of NitriSim [NitriSim 1 : without gas compostion correction ; NitriSim 2 : with gas composition correction. Correlations (Table 5) are C1 : Deront ; C2 : Saada ; C3 Alexander ; C4 : Marquez. **All values are in h^{-1}**.
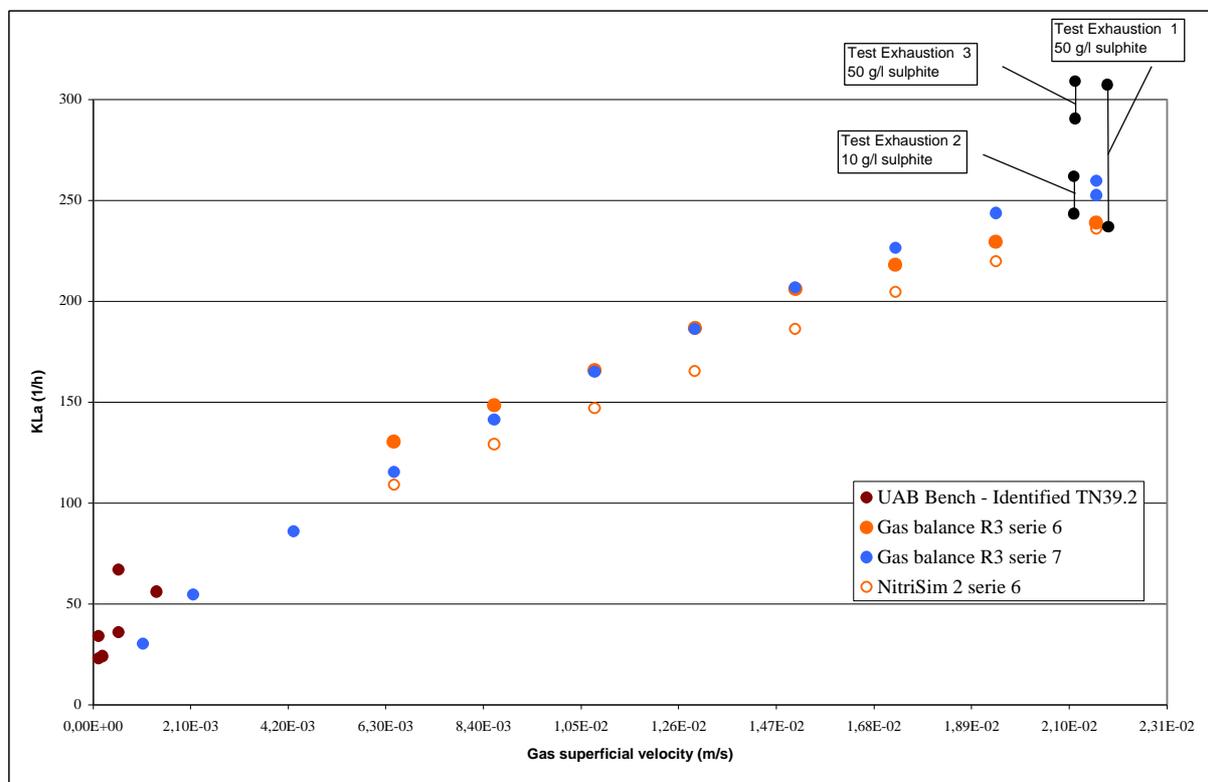

Figure 11 : K_La values calculated with relation 3.
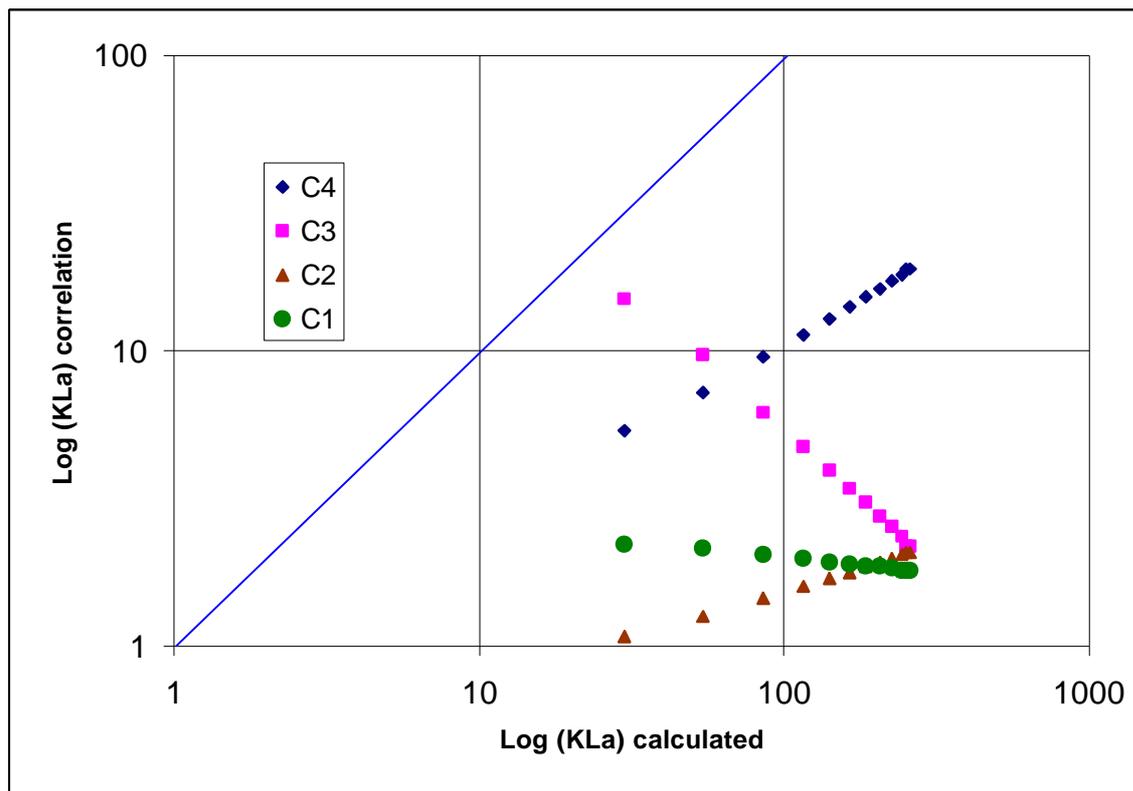
Figure 12 : $K_L a$ calculated in LGCB column compared to correlations for series S7. C1 : Deront ; C2 : Saada ; C3 Alexander ; C4 : Marquez. The parameters of the correlations used are those reported in Table 5.

The relation R3 is in principle more accurate than the R1 (or R2) relation as it takes into account the variation of the composition of the gas phase. The $K_L a$ values calculated with the R3 relation are about 23% higher than with R1 relation.

The $K_L a$ values identified with the NitriSim model (NitriSim 1 and NitriSim 2) are under the values obtained with the relations. It must be kept in mind that with NitiSim, a 10-tanks in series column was used, what is slightly different of a perfect plug-flow. That can be the reason of the differences observed. The differences are not constant. They are higher with low gas flow rates ($K_L a$ value identified with the NitriSim model is 85% of this calculated with the relation).

In Figure 12, the $K_L a$ values calculated with the correlations are plotted in a logarithmic scale and compared to the values calculated with the relation R3. The values calculated with the 4 corelations are 10 to 100 times lowers than those calculated with the relations or identified with NitriSim. More over, it is evident that the correlations itselves give different values of $K_L a$ for the sames operating conditions. It must also be noticed that for C1 and C3 correlation, the $K_L a$ increase with the decrease of the gas flow rate.

It must be kept in mind that these correlations were used with parameters identified for other fixed bed columns (Table 5). It is possible that with other parameters, the correlation could fit the experimental results obtained with the C50 column. The identification of such new

parameters for the correlations will require to performed experiments for a larger range of gas and liquid flows rates, and at least for the C1 correlation, to measure the pressure drop.

In Figure 11 it is interesting to notice that the K_La values estimated for the UAB nitrifying bench columns (Table 7) are in accordance with the value obtained with the C50 column (wich design is comparable to the UAB bench nitrifying columns), even if the liquid flow rates are not the same. These results must be checked for liquid superficial velocity comparable to the UAB bench column.

VI Conclusion

The gas-sulphite method for K_La measurement was developed and successfully applied for a fixed bed reactor.

The method must be completed by checking the repeatability of the measurements.
Some improvement are also required :

▪ The hydrodynamic of the C50 must be investigated in order to check an to understand the variation of the gas fraction at the output of the column. This implies to study the Residence Time.

▪ The K_La measured with the gas sulphite method must be compared to another technique such as the electrode method, which is a non coalescent technique. In order to use a technique base on the liquid flow (such as electrode technique), the knowledge of the hydrodynamic of the C50 column is required.

▪ The pressure drop is a parameter that would be measured. It could enables to establish a correlation for the K_La prediction. It must be outlined that the correlation of Deront et al (1998) which includes pressure drop is the less inaccurate of the four correlation used.

The correlations of the literature that we have used are inaccurate for the C50 column. Further measurements will enable to identify new parameters for these models and to check if the inaccuracy is related to the expression of the model or to its parameters, which are dependant of the design and the operating conditions of the column.

In order to establish a predictive correlation for the K_La the effect of :

▪ Liquid flow rate (liquid superficial velocity),

▪ Gas flow rate (gas superficial velocity),

▪ Column design (comparison of C50 and C150 column),

must be studied. This will also answer the question of how this new system and the data obtained can be combined and extrapolated with the data from UAB columns.

It must be outlined that the characterisation of gas-liquid transfer is a very complex problem, depending of both design parameters (particles diameter, diameter of the column, height of the column) and operation variables (flow rates,…) probably explaining important discrepancies between the correlations which are proposed in the literature. This justifies a specific study in order to predict (and control) the gas exchange intensity which becomes a key factor in nitrifying columns in some conditions.

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