Respirometric estimation of the oxygen affinity constants for biological ammonium and nitrite oxidation

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Abstract: The nitrification process (ie biological ammonium oxidation to nitrate) is a two-step process with nitrite as an intermediate product. As it is an aerobic process, its kinetics is highly dependent on the dissolved oxygen (DO) concentration in the medium. However, the influence of this limitation on the nitritation (first step) is shown to be less important than in the nitratation (second step). This dependence on DO concentration is generally described using a Monod-type kinetics with $K_O$ as the oxygen affinity constant. In this work, a procedure for the calculation of both affinity constants is presented. This procedure is based on monitoring the DO drop in the reactor when external aeration is stopped and the biomass is consuming without substrate (ammonium or nitrite) limitations. This methodology includes the contemplation of the oxygen transfer from the atmosphere, the response time of the DO probe and the inhibition of the nitratation step with sodium azide when estimating $K_{OA}$ (nitritation oxygen affinity constant). The results obtained are $K_{OA} = 0.74 \pm 0.02 \text{ mg O}_2 \text{ dm}^{-3}$ and $K_{ON} = 1.75 \pm 0.01 \text{ mg O}_2 \text{ dm}^{-3}$. Moreover the influence of the aforementioned considerations on the estimated $K_O$ values is also discussed.

Keywords: nitratation; nitritation; oxygen affinity constants; partial nitrification; respirometry

1 INTRODUCTION
The Biological Nitrogen Removal (BNR) process is the most common technology for removing ammonium from wastewater. This process is divided into two steps: ammonium oxidation to nitrate (nitrification) and nitrate reduction to nitrogen gas (denitrification). Nitrification is also a two-step process, where ammonium is firstly oxidised to nitrite by ammonium-oxidising biomass (AOB). This process is called nitritation and its stoichiometry is:

$$\text{NH}_4^+ + 3/2 \text{O}_2 \rightarrow \text{NO}_2^- + 2 \text{H}^+ + \text{H}_2\text{O} \quad (1)$$

Secondly, nitrite is oxidised to nitrate by nitrite-oxidising biomass (NOB). This process is called nitratation and its stoichiometry is:

$$\text{NO}_2^- + 1/2 \text{O}_2 \rightarrow \text{NO}_3^- \quad (2)$$

The total oxygen required in the whole nitrification process is 4.57 mg O$_2$ per mg N-NH$_4^+$ oxidised. The first step requires 3.43 mg O$_2$ mg$^{-1}$ N-NH$_4^+$ and the second step 1.14 mg O$_2$ mg$^{-1}$ N-NH$_4^+$. The nitrification process occurs under aerobic conditions and, as such, the kinetics of this process is strongly influenced by the dissolved oxygen (DO) concentration in the medium. The nitrification kinetics’ dependence on the DO concentration is generally described using the Monod expression (eqn (3)). As can be deduced, the $K_O$ represents the DO concentration at which the nitritation or nitratation rate is half of the maximum nitritation or nitratation rate.

$$r = r_{\text{max}} \frac{[\text{DO}]}{K_O + [\text{DO}]} \quad (3)$$

where:

- $r$ = nitritation or nitratation rate (mgN mg VSS$^{-1}$ d$^{-1}$)
- $r_{\text{max}}$ = maximum nitritation or nitratation rate (mg N mg VSS$^{-1}$ d$^{-1}$)
- $[\text{DO}]$ = dissolved oxygen concentration (mg O$_2$ dm$^{-3}$)
- $K_O$ = AOB or NOB affinity constant for DO (mg O$_2$ dm$^{-3}$)

The values of the $K_{OA}$ and $K_{ON}$ (affinity constants for nitration and nitratation, respectively) were generally taken from the literature instead of being estimated. However, these values have recently gained a lot of importance, particularly in view of modelling...
tasks, since new alternatives to the classical BNR at low DO values have appeared. These technologies aim at partial inhibition of the second step of nitrification. Hence, the nitratation step is favoured with respect to the nitrification step and nitrite is accumulated. This technology is called partial nitrification or nitrification via nitrite and could suppose a 25% reduction of the total oxygen requirements as well as a reduction in the amount of sludge produced.

Several strategies have been tested to achieve partial nitrification. The main difference between them is how to prevent the nitration step from occurring without affecting the nitratation step. One methodology is based on the lower NOB affinity for the DO compared with AOB.\textsuperscript{1–3} Thus, partial nitrification can be achieved by choosing a certain DO set-point where the nitratation rate is not oxygen limited as much as the nitratation rate. Reliable values for the oxygen affinity constants of the two processes are required to correctly model this methodology. Other possible methodologies are the SHARON process, which makes use of the different growth rates of AOB and NOB at high temperatures (30–35 °C) by working at a hydraulic retention time (HRT) higher than the growth rate of NOB but lower than the AOB (about 1 day) and without sludge retention.\textsuperscript{4,5} Finally, the application of higher inhibition of NOB by free ammonia (FA) than the AOB has also been described in the literature as a procedure for partial nitrification.\textsuperscript{6,7}

As the oxygen supply represents a very important cost in most wastewater treatment plants (WWTP), the DO concentration is usually maintained at a low level (around 2 mg O₂ dm\(^{-3}\)). The oxygen limitation is known to have more influence on nitrification than on the heterotrophic processes since both \(K_O\) values for nitrification are described to be higher than the ones proposed for heterotrophic processes. Then, knowing the values of both \(K_O\) constants can help the WWTP manager to choose a proper DO set-point in periods when nitrification is decreasing (ie winter).

\(K_O\) is generally estimated in two different ways: (a) calculating a certain process rate at different oxygen values,\textsuperscript{8} and (b) monitoring the DO drop in the reactor when external aeration is stopped. This second procedure was successfully applied by Wiesmann\textsuperscript{9} for \(K_{ON}\) estimation and an extension of this technique was employed in this work for estimating both \(K_{OA}\) and \(K_{ON}\). Apart from a different mathematical approach to the problem, the main modifications included were the contemplation of the oxygen transfer from the atmosphere, the response time of the DO probe and the inhibition of the nitrification step with sodium azide when estimating \(K_{OA}\).

\[ \frac{dS_0}{dt} = k_La \cdot [S_0^* - S_0(t)] - OUR_{END} - OUR_{EX} \]  \(4\)

where:

\[ k_La = \text{global oxygen mass transfer constant (d}^{-1}) \]
\[ S_0^* = \text{dissolved oxygen saturation level (mg O}_2\text{ dm}^{-3}) \]
\[ S_0 = \text{dissolved oxygen concentration (mg O}_2\text{ dm}^{-3}) \]
\[ OUR_{END} = \text{endogenous OUR value (mg O}_2\text{ dm}^{-3} \text{ d}^{-1}) \]
\[ OUR_{EX} = \text{exogenous OUR value (mg O}_2\text{ dm}^{-3} \text{ d}^{-1}) \]

The experiments for the assessment of the oxygen transfer through the liquid–gas surface were developed in the same experimental set-up as described above except for the respirometric vessel which was substituted for an Erlenmeyer flask of 1 dm\(^3\) volume.

2.2 Nitrifying biomass

The sludge used in this work was a biomass particularly enriched in nitrifying microorganisms because it was grown in a pilot plant fed with a very low COD/N ratio.\textsuperscript{11}

2.3 Procedure

The procedure developed in this work consisted of monitoring the DO drop in the respirometric vessel when the aeration was turned off and the biomass was consuming without substrate (ammonium or nitrite) limitations. A pulse of substrate was added to the respirometer and, once the maximum rate was reached, the aeration was stopped. At this moment, the DO in the liquid phase sharply decreased because of the oxygen consumption being linked to the substrate consumption. This oxygen consumption rate

corresponded to the maximum OUR assuming that no substrate (ammonium or nitrite) limitations existed. It was essential to avoid any substrate limitation (except from oxygen) for a reliable estimation. The nitritation or nitratation rate decreased as the DO concentration also decreased in the respirometer because of oxygen limitations. The lower the DO level was, the more important the oxygen limitation effect became (eqn (3)).

According to eqn (4), the system without either external aeration or substrate limitations should be described with:

\[
\frac{dS_o}{dt} = -\text{OUR}_\text{END} - \text{OUR}_\text{MAX}
\]  

(5)

Nevertheless, this expression is not valid in most of the experimental set-ups used, since the effect of oxygen limitation and the oxygen transfer through the liquid–gas surface need to be considered. This transfer is generally neglected when compared to the oxygen transfer due to the system external aeration. However, in some open and stirred systems without external aeration, this transfer may acquire enough importance to be considered. Although the liquid–gas surface area was minimised as much as possible during the experiments, it will be demonstrated below that this transfer should not be ignored. During the DO drop, the DO reached levels close to zero, which implies high levels of driving force for oxygen transfer through the liquid–gas surface: \([S_o^* - S_o(t)]\). Thus, the expression that better describes the system is:

\[
\frac{dS_o}{dt} = k_L a_\text{SUP} \cdot [S_o^* - S_o(t)] - (\text{OUR}_\text{END} + \text{OUR}_\text{MAX}) \cdot \frac{S_o}{K_O + S_o}
\]  

(6)

where \(k_L a_\text{SUP}\) is the global oxygen transfer constant through the liquid–gas surface and \(\text{OUR}_\text{MAX}\) is defined as a function of the substrate used (eqns (7a), (7b))

\[
\text{OUR}_\text{MAX} = \frac{3.43 - Y_A}{Y_A} \cdot \mu_{\text{MAX}_A} \cdot X_A \text{ for AOB}  
\]  

(7a)

\[
\text{OUR}_\text{MAX} = \frac{1.14 - Y_N}{Y_N} \cdot \mu_{\text{MAX}_N} \cdot X_N \text{ for NOB}  
\]  

(7b)

where \(Y\) is the biomass yield, \(X\) is the biomass concentration and \(\mu_{\text{MAX}}\) is the maximum specific growth rate.

2.4 Parameter estimation

Modelling, simulation and parameter estimation were performed using MATLAB 6.5 (The MathWorks, Natick, MA). The differential equations were solved using an explicit Runge-Kutta formula. Parameter estimation was carried out by using the Nelder–Mead Simplex search method, where the weighted sum \(J\) (eqn (8)) of squared errors between model outputs \(y(t_k, \theta)\) and the measured outputs \(y_M(k)\), with \(W_k\) as weighting matrix was minimised:

\[
J = \sum_{k=1}^{N} [y(t_k, \theta) - y_M(k)]^T W_k [y(t_k, \theta) - y_M(k)]  
\]  

(8)

where \(N\) is the number of measurements and \(T\) is transposed.

For the parameter estimation confidence intervals assessment, the Fisher Matrix Information (FIM) was used. If \(Q_k\) is equal to the inverse of the measurement error covariance matrix, the FIM is defined as:

\[
\text{FIM} = \sum_{k=1}^{N} Y_k^T Q_k Y_k  
\]  

(9)

The FIM matrix summarises the quantity and quality of information obtained in each experiment because it considers the output sensitivity functions and the measurement errors of an experimental data (ie accuracy of an experiment). Assuming white measurement noise and no model mismatch, the inverse of the FIM provides the lower bound of the parameter estimation error covariance matrix, which can be used for assessing the estimation uncertainty of \(\theta_O\) (optimal estimated parameters).

\[
\text{COV}(\theta_O) \geq \text{FIM}^{-1}  
\]  

(10)

3 RESULTS

3.1 \(k_L a_\text{SUP}\) assessment

As aforementioned, the oxygen transfer through the liquid–gas surface due to the stirring process must be taken into account. This transfer depends on the volumetric oxygen mass transfer constant \((k_L a_\text{SUP})\), which derives from a multiplication of \(k_L\) (surface oxygen transfer constant) and \(a\) (ratio between surface area and volume of the reactor). In this work, \(k_L\) was estimated through an experiment where the apparent endogenous OUR \((\text{OUR}^\text{APP}_\text{END})\) was measured at different values of \(a\). It was calculated in a previous experiment as the slope of the DO decrease in the reactor without external aeration and without external substrate. The experimental profiles obtained are plotted on Fig 1. This experiment was conducted under the same operational conditions (\(\text{pH}\), temperature and stirring) as in the \(K_O\) estimation experiments, except for the vessel which was substituted for an Erlenmeyer (1 dm\(^3\)) flask to obtain different values of \(a\).

As can be seen in Fig 1, the lower the parameter \(a\), the higher the apparent endogenous OUR value. This is understandable since a decrease in the contact area will imply less oxygen transferred from atmosphere and the error in estimating the oxygen consumption of the biomass will be lower. Hence, the intercept value of the regression (the \(\text{OUR}^\text{APP}_\text{END}\) for \(a = 0\)) can be considered as the ‘real’ endogenous value (ie without surface transfer).
between the same limits of DO (from 6.6 to 6 mg $\text{O}_2\text{ dm}^{-3}$) and oxygen transfer). Then, OUR$_{\text{APP}}$ can be described as a function of the parameter $a$, according to eqn (11):

$$\text{OUR}_{\text{APP}}(a) = \text{OUR}_{\text{REAL}} + k_1 \cdot a \cdot \text{SUP} \cdot (S_O^+ - S_O)$$

where $k_1$ can be calculated from the slope of the regression above (eqn (12)):

$$k_1 = \frac{\text{slope}}{(S_O^+ - S_O)}$$

OUR$_{\text{APP}}$ values for each value of $a$ were calculated between the same limits of DO (from 6.6 to 6 mg $\text{O}_2\text{ dm}^{-3}$ approximately). $S_O^+$ is 8.49 mg $\text{O}_2\text{ dm}^{-3}$ at 25°C. Then, if the driving force $(S_O^+ - S_O)$ was assumed to be 2.2 (obtained from 8.5 - 6.3), the value of $k_1$ calculated was 8.33 m$^3$ m$^{-2}$ d$^{-1}$. Finally, as the measured parameter $a$ in the respirometric vessel employed in this work was 0.49 m$^2$ m$^{-3}$, the value of the $k_1 \cdot a \cdot \text{SUP}$ estimated was 4.08 d$^{-1}$. This value will be used below when $K_O$ is estimated.

3.2 DO probe time response

The time response of the DO probe is not a negligible parameter, particularly in fast experiments with sharp/sudden DO changes. The importance of this parameter arises in experiments with low data collection frequency. In this work, the time constant for the DO probe was calculated for a proper $K_O$ estimation, especially for the $K_O$ where the experiments performed accomplish the conditions aforementioned.

The DO probe time constant was estimated using positive and negative steps to the measured output (DO concentration). These steps were achieved with two different water solutions bubbled with air and nitrogen respectively. For example, the negative step was obtained with an instantaneous change of the DO probe submerged in the air-bubbled water to the nitrogen-bubbled water. Assuming that the DO probe behaves as a first order system, the DO profile obtained with this immediate change can be fitted to the next expression:

$$S_O = S_O^{\text{INITIAL}} + K \cdot (1 - e^{-t/\tau})$$

where:

$K = \text{absolute value of the step (mg O}_2\text{ dm}^{-3})$

$\tau = \text{DO probe time constant (s)}$

In this work, the DO probe time constant was calculated to be 5.8 s. Then, the measured DO values should be corrected according to:

$$S_O^{\text{CORR}}(t) = \frac{S_O^{\text{MEAS}}(t) - (1 - a) \cdot S_O^{\text{MEAS}}(t - 1)}{\alpha}$$

where:

$S_O^{\text{CORR}} = \text{corrected DO concentration (mg O}_2\text{ dm}^{-3})$

$S_O^{\text{MEAS}} = \text{measured DO concentration (mg O}_2\text{ dm}^{-3})$

$\alpha = \Delta t/(\Delta t + \tau)$ and $\Delta t = \text{data collection frequency}$

3.3 Nitratation inhibition with sodium azide

Nitratation inhibition is required for the correct calculation of $K_{OA}$. Otherwise, the measured OUR will correspond to the sum of the OUR due to ammonium oxidation and the OUR linked to the nitrite consumption produced during the nitratation step. Only the OUR related to the ammonium consumption should be used when estimating $K_{OA}$. The nitratation step was inhibited using sodium azide as described before. Nevertheless, a preliminary experiment was performed to ensure that the experimental concentration of sodium azide added only inhibited nitratation and had minimal effect upon nitratation (Fig 2).

According to Fig 2, when a pulse of 25 mg dm$^{-3}$ of nitrogen as ammonium was added without inhibitor (first pulse), it was possible to differentiate the two steps of the nitrification process. The nitratation step was slower than the nitritation step under the experimental conditions used in this work. The total oxygen consumption related to this pulse (corresponding to the area under the OUR profile) was 108.4 mg O$_2$. This indicated a global biomass yield for the nitrification of 0.23 mg COD$_X$ mg$^{-1}$ N, which is in the range of the reported values in the literature.

The second pulse corresponded to the simultaneous addition of ammonium (25 mg dm$^{-3}$ N-NH$_4^+$) and sodium azide (24 $\mu$M). At first glance, the second shoulder corresponding to the nitratation step was not observed, which could clearly indicate the occurrence of inhibition. Moreover, the oxygen consumed in this second pulse was 81.75 mg O$_2$. The ratio of this value on the oxygen consumed in the pulse without inhibition was 0.754 which was in agreement with the stoichiometric ratio: 0.750 (≈ 3.43/4.57). This value illustrates that the nitratation step is not inhibited at all with the amount of sodium azide added.
a third pulse of nitrite was added to confirm the nitratation inhibition and no response in terms of oxygen consumption was observed.

### 3.4 $K_{OA}$ and $K_{ON}$ estimation results

The experimental DO profiles obtained without either external aeration or substrate limitations are depicted in Figs 3 (AOB biomass) and 4 (NOB biomass). These experimental DO drops could be described using the ordinary differential equation (eqn (6)). $K_{OA}$ and $K_{ON}$ were estimated by fitting the experimental DO profiles to eqn (15). $K_{O}$ estimation results obtained as an average of both experiments (A,B) for each of the processes are:
$K_{OA} = 0.74 \pm 0.02 \text{ mg O}_2 \text{ dm}^{-3}$ and $K_{ON} = 1.75 \pm 0.01 \text{ mg O}_2 \text{ dm}^{-3}$. The parameters were estimated for a confidence level of 95%. The parameter estimation error predicted for $K_{OA}$ using the FIM methodology was twice the one predicted for $K_{ON}$. This is understandable since the experiments with nitrite as substrate were slower and, then, the data collection and the amount of information increased. However, in both cases, the parameter estimation errors are very small, so the estimated $K_O$ values can be considered quite reliable.

Table 1 compares the estimated $K_O$ values with different $K_O$ values found in the literature. As can be seen, the values estimated in this study were considerably higher than the default ones used in the classical Activated Sludge Model No 1. This fact may cause an important error when estimating the values of $\mu_{MAX}$ and $K_S$ from respirometric batch experiments using 0.4 as the $K_O$ value.

$K_O$ values neglecting surface oxygen transfer were estimated to confirm that this transfer should be taken into account. The $K_{OA}$ obtained was $0.75 \pm 0.02 \text{ mg O}_2 \text{ dm}^{-3}$ and the $K_{ON}$ was $2.320 \pm 0.015 \text{ mg O}_2 \text{ dm}^{-3}$. As expected, the oxygen transfer neglect implied an overestimation of the constants, especially when estimating $K_{ON}$. The reason is that the $K_{ON}$ estimation experiments last longer and the oxygen transfer effect becomes more important.

Table 1. $K_O$ values obtained in this study and from the literature

<table>
<thead>
<tr>
<th>Affinity constant for DO (mg O$_2$ dm$^{-3}$)</th>
<th>Temperature (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOB ($K_{OA}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.74 ± 0.02</td>
<td>25</td>
<td>This study</td>
</tr>
<tr>
<td>1.45</td>
<td>35</td>
<td>4</td>
</tr>
<tr>
<td>1.66$^a$</td>
<td>30</td>
<td>8</td>
</tr>
<tr>
<td>0.6</td>
<td>25</td>
<td>9</td>
</tr>
<tr>
<td>0.5–2</td>
<td>25</td>
<td>18</td>
</tr>
<tr>
<td>0.4</td>
<td>25</td>
<td>19</td>
</tr>
<tr>
<td>0.16</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>0.3</td>
<td>28</td>
<td>21</td>
</tr>
<tr>
<td>NOB ($K_{ON}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.75 ± 0.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Obtained at 24 g NaCl dm$^{-3}$.

$K_O$ values neglecting the DO probe time response were also estimated to assess the effect of this parameter. The results showed that neglecting the DO probe time response implied a significant underestimation of the $K_O$ values because the values obtained were $K_{OA} = 0.49 \pm 0.02 \text{ mg O}_2 \text{ dm}^{-3}$ and $K_{ON} = 1.640 \pm 0.01 \text{ mg O}_2 \text{ dm}^{-3}$. This response time is so important because the experimental profiles show a sudden and sharp decrease which is faster than the time response of the probe.

In relation to the values of the $K_O$, the value of $K_{ON}$ obtained was more than twice the value of the $K_{OA}$. This indicated that the nitrification step is more influenced by oxygen limitations than the nitritation step. According to these values, one could evaluate which DO set-point would be more favourable to accomplish partial nitrification. This effect is shown in Fig 5, where a simulation of the percentages of the maximum nitritation and nitrification rates achieved at different DO concentrations are plotted. For example, for a DO value of 2 mg O$_2$ dm$^{-3}$ (typical WWTP set-point), the nitritation rate would be reduced to 74% of its maximum rate without limitations and the nitrification rate would be reduced to 53% of the maximum nitrification rate. Once this ratio is known, the value of both the maximum nitritation and nitrification rates should be calculated as a function of the operational conditions (such as temperature and pH) to estimate the operational nitritation and nitrification rates in the system.

As can be observed, the lower the DO value, the more the nitritation is favoured over nitrification because, at low DO values, the effect of the $K_O$ is more significant in the second step. Apparently, an optimal operation procedure to achieve partial nitrification would require low DO values (assuming that the values of both the maximum nitritation and nitrification rates are close). Moreover, the aeration costs will diminish while decreasing the oxygen set-point. However, low DO values also imply low nitrification rates and, hence, larger reactor volumes. After all, a balanced decision should be made taking into account all these features.
3.5 Effect of oxygen limitations in respirometric batch experiments

Finally, an example of the oxygen limitation effect upon respirometric batch experiments is shown to explore the importance of this limitation when interpreting the measured OUR profile. This example was developed using the LFS respirometer previously described. A pulse of 10 mg dm\(^{-3}\) of N-NH\(_4^+\) was added with a low airflow so that, when the biomass consumed at its maximum rate, the DO in the reactor dropped to quite low values. Both the DO and the OUR profiles are plotted in Fig 6.

As can be seen in Fig 6, the OUR value did not instantaneously reach the maximum value after the ammonium pulse was added (\(t = 80\) min), but increased progressively. This transient period to reach the maximum OUR value has already been discussed in the literature with nitrifying biomass\(^{10,22}\) and cannot be described according to Monod kinetics. As this transient period was finishing, a maximum peak was attained and, then, the OUR decreased down to steady value as a consequence of oxygen limitations. The OUR value remained stable (around 2.2 mg O\(_2\) dm\(^{-3}\) min\(^{-1}\)) as long as the DO did not change (ie there were no ammonium limitations).

Hence, this initial unusual sharp pointed peak observed in the first shoulder of the OUR profile should not be attributed to experimental error but to oxygen concentration. Similar (but smaller) sharp peaks can be obtained in respirometric batch experiments when the DO reaches values lower than 3 (Fig 2). The \(K_{OA}\) value found in this work (0.74 ± 0.02 mg O\(_2\) dm\(^{-3}\)) is in agreement with this observation.

In addition, the oxygen limitation effect could also be observed in the second shoulder of the OUR profile (nitratation step). When the DO level was at its lowest value (around 0.5 mg O\(_2\) dm\(^{-3}\)), this step was extremely limited and, afterwards, as the DO rose because the nitritation step finished, the OUR related to the nitratation step increased considerably (Fig 6). The fact that the nitratation step was more sensitive to oxygen limitations is in agreement with the \(K_O\) values previously estimated (\(K_{ON} = 1.75 ± 0.01\) mg O\(_2\) dm\(^{-3}\)).

Finally, the dependence of these unusual peaks observed in Fig 6 on the oxygen limitations was simulated. Four different simulations were run with the same initial pulse addition (30 mg N-NH\(_4^+\) dm\(^{-3}\)) and different \(k_La\) values so that the air transfer and the bottom DO level were higher in each simulation. A classical two-step nitrification model described elsewhere\(^{23–25}\) with standard parameters and a transient period of 1.3 min was used for simulations. The DO and OUR profiles obtained (Fig 7) showed that the sharp peak observed in the first shoulder disappeared at the same time as the oxygen limitations were reduced (higher \(k_La\)). Moreover, the higher the \(k_La\), the faster the pulse was consumed because both the nitritation and the nitratation rates were not oxygen limited as much.
The OURs related to the nitration step and to the nitratation step are also depicted in Fig 7. The effect of oxygen limitations in the second step can be clearly seen, mainly in the simulation with the lowest $k_{a,1}$ value. In this simulation, the behaviour of this second shoulder was very close to the one experimentally observed (Fig 7).

4 CONCLUSIONS

(1) An extension of the procedure employed by Wiesmann9 for the $K_{ON}$ estimation was employed for both $K_{OA}$ and $K_{ON}$ estimation. The results obtained were $K_{OA} = 0.74 \pm 0.02 \text{ mg O}_2 \text{ dm}^{-3}$ and $K_{ON} = 1.75 \pm 0.01 \text{ mg O}_2 \text{ dm}^{-3}$.

(2) Hence, the nitratation step is more influenced by oxygen limitations than the nitration step. Depending on the DO set-point chosen and taking into account the maximum nitration and nitratation rate, one can expect to achieve partial nitrification by favouring the nitration step over the nitratation step.

(3) These $K_{O}$ values are considerably higher than the default ones used in the classical Activated Sludge Model No 1.19 This fact could influence the estimated values of $\mu_{MAX}$ and $K_S$ from respirometric batch experiments using 0.4 as $K_O$.

(4) It has been demonstrated that oxygen transfer from the atmosphere should be taken into account when using open and stirred systems such as the one used in this work. Otherwise, the $K_O$ values would be overestimated.

(5) To take into account this oxygen transfer, the volumetric oxygen transfer constant from the atmosphere ($k_{a,SUP}$) was calculated by measuring the endogenous OUR value at different surface to volume ratios in the reactor.

(6) The DO probe time response was also estimated for a proper $K_O$ estimation. Neglecting the DO probe time response implied an underestimation of the $K_O$ values because of the sharp experimental DO decrease which is faster than the time response of the probe.

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