

Improved Theoretical Identifiability of Model Parameters by Combined Respirometric – Titrimetric Measurements. A Generalisation of Results

Britta Petersen^{1,2}, Krist Gernaey¹ and Peter Vanrolleghem^{1,#}

¹ BIOMATH Department, University of Gent, Coupure Links 653, B-9000 Gent (Belgium)

² EPAS NV, Technologiepark 3, B-9052 Gent-Zwijnaarde (Belgium)

Corresponding author : Tel. +32 9 264 59 32, Fax +32 9 223 49 41, E-mail: Peter.Vanrolleghem@rug.ac.be

Abstract. The theoretical identifiability of the two-step nitrification model was studied with respirometric and titrimetric outputs. Most remarkable result is that the autotrophic yield becomes uniquely identifiable when combined data are considered. Furthermore, it is illustrated how the identifiability results can be generalised by applying a set of ASM1 matrix based generalisation rules. It appears that the identifiable parameter combinations can be predicted based on knowledge of the process model under study (in ASM1-like matrix representation), the measured variables and the biodegradable substrate considered.

Introduction

Monod-type growth kinetics are most often applied to describe wastewater degradation processes [6]. The evaluation of the theoretical identifiability of model parameters prior to practical model application, e.g. in the frame of parameter estimation or model calibration, is very important, and is based on the model structure and on the measured variables [3]. Perfect noise-free data are assumed in a theoretical identifiability study whereas in practice the data may be noise corrupted. As a result, parameters may be unidentifiable in practice, even if they are theoretically identifiable [7].

In a study on heterotrophic substrate degradation via the Monod model [7], measurements of both substrate and biomass were assumed to be available, and in that case all parameters were proven to be theoretically identifiable. In another study growth was neglected in the model, and oxygen uptake rate data were considered [3]. In the latter situation only certain parameter combinations were theoretically identifiable. Furthermore, the theoretical identifiability of Monod kinetics for a denitrification model was analysed assuming steady state with respect to growth [1]. These results also confirmed that depending on the measured state variables (nitrate, nitrite, carbon substrate) different parameter combinations were identifiable.

The theoretical identifiability analysis of the two-step nitrification process (Monod kinetics) considering outputs from respirometry (oxygen uptake rates, r_O) and titrimetry (cumulative proton production, H_p) is the objective of this study. Model structures with and without biomass growth are considered. The theoretical identifiability was studied by using the Taylor series expansion method, and symbolic manipulations were carried out with MAPLE V. Finally, the results of the identifiability study are generalised based on the stoichiometric matrix of the Activated Sludge Model No.1 [6].

Theoretical background

The basic assumptions of the Taylor series expansion approach are that the output vector and its derivatives with respect to time at the initial time $t=0$ are assumed to be known and unique. The identifiability analysis is thus reduced to a determination of the solutions for the parameters in a set of (non-linear) algebraic equations. A sufficient condition for the model to be theoretically identifiable is that a unique solution exists for the parameters [9,11].

The model under study (Table 1) is based on ASM1 [6], with some modifications [5]. Nitrification takes place in two steps: (1) oxidation of ammonium (S_{NH}) to nitrite (S_{NO_2}) and (2) oxidation of nitrite to nitrate (S_{NO_3}). Both nitrification steps can be monitored by oxygen uptake measurements whereas it is only during the first step that protons are produced. Thus, only the first step can be characterised by proton production measurements. Measurements of oxygen uptake rate (r_O) can be carried out via respirometry [2,10], and proton production (H_p) can be quantified via a titrimetric technique [4].

Figure 1 illustrates a typical data set obtained following the addition of S_{NH} to a batch reactor filled with activated sludge at $t=0$. Concentration profiles were simulated using the model of Table 1. The S_{NH} concentration decreases while S_{NO_2} builds up because, for this example, the second nitrification step is slower than the first step. The oxidation of S_{NH} results in a certain oxygen uptake rate (defined as exogenous respiration rate, $r_{O,ex}$). The build-up of S_{NO_2} causes the tail on the $r_{O,ex}$ profile. In the titrimetric method the pH of the liquid is controlled around a constant pH setpoint. Thus, in the case of nitrification acid is produced in the first step, and base has to

be added to keep the pH constant. This results in the cumulative base addition curve in Figure 1 (directly proportional to the cumulative proton production).

Table 1. Model used for interpretation of the respirometric and titrimetric data

Comp. (meas., i; substr., k)→ Process (j) ↓	1. X	2. S _S	3. S _O	4. S _{NH}	5. S _{NO2}	6. S _{NO3}	7. H _p	Process rate
1. Growth on S _S	1	$-\frac{1}{Y_H}$	$-\frac{1-Y_H}{Y_H}$	$-i_{XB}$			$\frac{i_{XB}}{14}$	$\mu_{\max H} \frac{S_S}{K_S + S_S} X$
2. Nitrification step 1	1		$-\frac{3.43 - Y_{A1}}{Y_{A1}}$	$-\frac{1}{Y_{A1}} - i_{XB}$	$\frac{1}{Y_{A1}}$		$\frac{i_{XB}}{14} + \frac{1}{7Y_{A1}}$	$\mu_{\max A1} \frac{S_{NH}}{K_{SA1} + S_{NH}} X$
3. Nitrification step 2	1		$-\frac{1.14 - Y_{A2}}{Y_{A2}}$		$-\frac{1}{Y_{A2}}$	$\frac{1}{Y_{A2}}$		$\mu_{\max A2} \frac{S_{NO2}}{K_{SA2} + S_{NO2}} X$

Results

First, the theoretical identifiability of the two-step nitrification model was studied for separate outputs of $r_{O,ex}$ and H_p data, considering a model structure in which biomass growth did not take place. This means that the first column in Table 1 is not considered (X is constant) and that $i_{XB}=0$. Second, a model structure was studied in which biomass growth was included.

The theoretical identifiability was dealt with separately for the first and the second nitrification step, similar to an earlier study of a double Monod model with two carbon substrates added at $t=0$ [3]. However, there are two major differences between the two-step nitrification process and this double Monod example: (1) At $t=0$ the concentration of S_{NO2} is zero. Hence, only information on the kinetics of the first nitrification step is available at $t=0$; (2) the two nitrification steps are linked in the way that S_{NO2} is produced from the first step, i.e. as long as S_{NH} is present a time varying input of S_{NO2} exists. The study of the theoretical identifiability was therefore approached as follows. First, $t=0$ was considered and the identifiability of the first step was analysed. Secondly, it was assumed that S_{NH} was completely eliminated from the mixed liquor at a certain point $t>0$ (in Fig. 1 about $t=60$ min). At this point $S_{NH}=0$ and thus S_{NO2} is no longer produced. However degradation of S_{NO2} still takes place and as a consequence the identifiability of the second nitrification step can be studied. Thus, this is an example in which later observations ($t>0$) can give complementary information on possibly identifiable parameter combinations [9,11].

The full equations and solutions of the identifiability study are not given here due to their complexity (especially in the case where growth is included) and lack of space. The complete and detailed study will be described elsewhere [8]. Here, only the final results of the study are listed in Table 2. Important to notice is that $\mu_{\max A1}$ and X can be separated when growth is considered. Moreover, an extra term including the parameter i_{XB} (incorporation of S_{NH} during growth) appears in the parameter combinations for $S_{NH}(0)$ and K_{SA1} .

It was assumed that measurements of $r_{O,ex}$ and H_p are independent and measured simultaneously in the same system. Hence, the information on identifiable parameter combinations based on $r_{O,ex}$ and H_p data separately, can be combined in the search for possibly new and improved parameter identification with combined data. One should remember that improved identifiability can not be expected for the parameters of the second nitrification step since H_p measurements only give information on the first step. The important result of combining $r_{O,ex}$ and H_p data is that the biomass yield Y_{A1} becomes uniquely identifiable. For a model including growth i_{XB} is assumed known. It appears that Y_{A1} is defined by the ratio between the stoichiometric factors relating $r_{O,ex}$ and the first derivative of H_p to degradation of S_{NH} . The identification of Y_{A1} will result in a unique identification of Y_{A2} as well as long as $S_{NO2}(0)=0$ [8].

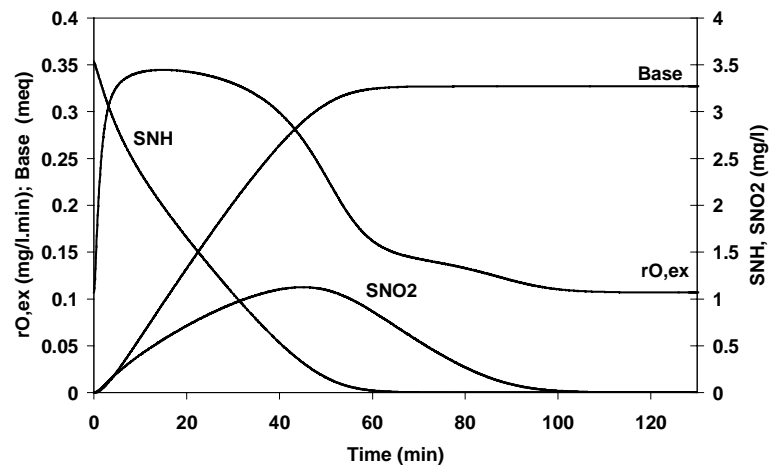


Figure 1 Model example of two-step nitrification [5]

Table 2. Schematic overview of the theoretically identifiable parameter combinations for nitrification step 1 and 2, depending on the available measurement(s) and the model structure

Process (j)	Nitrification step 1			Nitrification step 2
	r _O	Hp	r _O + Hp	r _O
Measurement (i) → Model structure ↓				
No growth	$\frac{3.43 - Y_{A1}}{Y_{A1}} \mu_{\max A1} X$ $(3.43 - Y_{A1}) K_{SA1}$ $(3.43 - Y_{A1}) S_{NH}(0)$	$\frac{2}{14} \frac{\mu_{\max A1} X}{Y_{A1}}$ $\frac{2}{14} K_{SA1}$ $\frac{2}{14} S_{NH}(0)$	$\frac{3.43 - Y_{A1}}{Y_{A1}} \mu_{\max A1} X$ $(3.43 - Y_{A1}) K_{SA1}$ $(3.43 - Y_{A1}) S_{NH}(0)$ $\frac{14}{2} (3.43 - Y_{A1})$	$\frac{1.14 - Y_{A2}}{Y_{A2}} \mu_{\max A2} X$ $(1.14 - Y_{A2}) K_{SA2}$ $(1.14 - Y_{A2}) S_{NO2}(0)$
Growth	$\frac{\mu_{\max A1}}{Y_{A1}} X(0)$ $\frac{3.43 - Y_{A1}}{1 + i_{XB} \cdot Y_{A1}} K_{SA1}$ $\frac{3.43 - Y_{A1}}{1 + i_{XB} \cdot Y_{A1}} S_{NH}(0)$	$\frac{\mu_{\max A1}}{14} \frac{X(0)}{Y_{A1}}$ $\frac{2 + i_{XB} Y_{A1}}{14(1 + i_{XB} Y_{A1})} K_{SA1}$ $\frac{2 + i_{XB} Y_{A1}}{14(1 + i_{XB} Y_{A1})} S_{NH}(0)$	$\frac{\mu_{\max A1}}{Y_{A1}} X(0)$ $\frac{3.43 - Y_{A1}}{1 + i_{XB} Y_{A1}} K_{SA1}$ $\frac{3.43 - Y_{A1}}{1 + i_{XB} Y_{A1}} S_{NH}(0)$ $\frac{2 + i_{XB} Y_{A1}}{14(3.43 - Y_{A1})}$	$\frac{\mu_{\max A2}}{Y_{A2}} X(0)$ $(1.14 - Y_{A2}) K_{SA2}$ $(1.14 - Y_{A2}) S_{NO2}(0)$

It appears possible to generalise the parameter identifiability results listed in Table 2 based on an ASM1 like stoichiometric matrix (Table 1). It appears that the identifiable parameter combinations can be predicted based on knowledge of the process under study, the measured component and the substrate component that is degraded. This generalisation is illustrated in Table 3, where v denotes the stoichiometric coefficient, j the process and i the measured component. If i is a component that is consumed (e.g. S_O , S_S) $v_{i,j}$ is negative whereas $v_{i,j}$ is positive if the measured component is a product (e.g. Hp , X). This is indicated in Table 3 with the factor f ($f = +1$ or -1). The substrate under study is denoted k and since k is always consumed $v_{k,j}$ gets a negative sign. In case two components are measured, the parameter combinations listed in Table 3 still hold but with the additional identifiable parameter combination $v_{i(1),j}/v_{i(2),j}$ where (1) and (2) indicate the two measured components respectively. The generalisation of Table 3 was confirmed with the identifiable parameter combinations listed in Table 2 [8], but also with examples from literature. E.g. in the study of Holmberg (1982) [7] it was shown that the parameters μ_{\max} , K_S , $S_S(0)$, $X(0)$ and Y_H were uniquely identifiable in case S_S and X measurements were available and biomass growth was considered. According to the generalisation (Table 3) and the model (Table 1) this means that $i(1)=1$, $i(2)=2$, $j=1$ and $k=2$ and the identifiable parameters can be found via :

- 1) $\mu_{\max,j}$, i.e. the growth rate related to process 1 : $\mu_{\max H}$.
- 2) $f v_{i,j} \cdot X$, both $i(1)$ and $i(2)$ can be considered : $v_{1,1} \cdot X = X$
- 3) $-f v_{i,j} / v_{k,j} \cdot K_j$: $-v_{1,1} / v_{2,1} \cdot K_1 \Rightarrow \left(1 \cdot \frac{1}{Y_H}\right) K_S = \frac{K_S}{Y_H}$
- 4) $-f v_{i,j} / v_{k,j} \cdot S_k(0)$: $-v_{1,1} / v_{2,1} \cdot S_2(0) \Rightarrow \frac{S_S(0)}{Y_H}$
- 5) $f v_{i(1),j} / f v_{i(2),j} \Leftrightarrow -v_{1,1} / v_{2,1} \Rightarrow 1 \cdot \frac{Y_H}{1} = Y_H$

Table 3. Generalisation of identifiable parameter combinations.

No growth ($i_{XB}=0$)	Growth
$f \cdot v_{i,j} \cdot \mu_{\max,j} \cdot X$	$\mu_{\max,j}$
$-f \cdot v_{i,j} / v_{k,j} \cdot K_j$	$f v_{i,j} \cdot X(0)$
$-f \cdot v_{i,j} / v_{k,j} \cdot S_k(0)$	$-f v_{i,j} / v_{k,j} \cdot K_j$
	$-f v_{i,j} / v_{k,j} \cdot S_k(0)$

Thus, since the biomass yield Y_H becomes identifiable (step 5) all the parameters $\mu_{\max H}$, K_S , $S_S(0)$, $X(0)$ and Y_H become identifiable by applying the generalisation rules, similar to the results of Holmberg [7].

Discussion

The theoretical identifiability of a two-step nitrification model was studied assuming that respirometric and titrimetric measurements were available. The study was carried out for a model structure that did not include biomass growth and a model structure where biomass growth was taken into account. With respect to parameter

identifiability, the difference between the two model structures was that the no-growth parameter combination including X , Y and μ_{\max} can be split up further into μ_{\max} on the one hand and a parameter combination including X and Y on the other hand when considering growth. Nitrification kinetic parameters have been estimated in earlier studies [2,10]. In these studies, however, the assumed theoretically identifiable parameter combinations were defined to be the ones related to no growth despite the fact that growth was considered explicitly in the model applied during parameter estimation. Thus, from a theoretical point of view, a wrong approach was taken. However, the experiments considered in these studies were all of short-term character where significant biomass growth is unlikely to take place. Indeed, to be able to practically identify the theoretically identifiable parameters based on a model including growth, the available data must show a significant increase of biomass, e.g. visible in an increase of $r_{O,ex}$. If the data do not reflect a significant growth μ_{\max} and X will be correlated in practice.

An important result of this study was that the autotrophic yield, Y_{A1} , becomes uniquely identifiable by combining respirometric and titrimetric data. It is not surprising that a unique identification of the biomass yield requires two kinds of measurements, since the yield in fact relates two measures that link how much biomass is produced per unit of substrate degraded. This was in fact already proven in [7] where combined measurements of biomass and substrate were assumed. The biomass yield becomes identifiable for the combined measurements because an additional parameter combination becomes identifiable compared to the single measurement cases. This additional parameter combination appears to be the ratio of the two stoichiometric factors that relate the respective measured variables to substrate degradation.

Finally and most substantially, it was proven and illustrated how it is possible to generalise the theoretical parameter identifiability based on an ASM1-like stoichiometric matrix. The identifiable parameter combinations can be predicted directly based on knowledge of the process under study, the measured component and the substrate component that is degraded. This generalisation is a very powerful tool since it reduces the time-consuming task of assessing the theoretical identifiability of process models described by Monod growth kinetics in an ASM1-like representation.

Conclusions

In this study the theoretical identifiability of the two-step nitrification model was studied considering respirometric and titrimetric data. The result of including biomass growth in the model was, not surprisingly, that the parameter μ_{\max} could be identified separately. However, more important was that the parameter identification improves when combined respirometric and titrimetric data are available since the autotrophic yield becomes uniquely identifiable. Finally, the results were generalised and it was shown how identifiable parameter combinations could be obtained directly from an ASM1-like matrix representing the model under study.

Literature

1. Bourrel, S.V., Babary, J.P., Julien, S., Nihtilä, M.T. and Dochain, D., Modelling and identification of a fixed-bed denitrification bioreactor, *System Analysis Modelling Simulation (SAMS)*, 30 (1998), 289-309.
2. Brouwer, H., Klapwijk, A. and Keesman, K.J., Identification of activated sludge and wastewater characteristics using respirometric batch experiments, *Water Res.*, 32 (1998), 1240 - 1254.
3. Dochain, D., Vanrolleghem, P.A. and Van Daele, M., Structural identifiability of biokinetic models of activated sludge respiration, *Water Res.*, 29 (1995), 2571-2578
4. Gernaey, K., Vanrolleghem, P.A. and Verstaete, W., On-line estimation of Nitrosomonas kinetic parameters in activated sludge samples using titration in-sensor-experiments, *Water Res.*, 32 (1998), 71 - 80.
5. Gernaey, K., Petersen, B., Ottoy, J.P. and Vanrolleghem, P.A., Activated sludge monitoring with combined respirometric – titrimetric measurements, Submitted to *Water Res.* (1999).
6. Henze, M., Grady, C.P.L. Jr., Gujer, W., Marais, G.v.R. and Matsuo, T., Activated sludge model No. 1, IAWQ Scientific and technical Report No. 1, London, 1987.
7. Holmberg, A., On the practical identifiability of microbial growth models incorporating Michaelis-Menten type nonlinearities, *Mathematical Biosciences*, 62 (1982), 23-43.
8. Petersen, B., Optimal experimental design for wastewater and sludge characterisation, Ph.D. thesis. Biomath department, University Gent, B-9000 Belgium. In preparation, 2000.
9. Pohjanpalo, H., System identifiability based on the power series expansion of the solution, *Mathematical Biosciences*, 41 (1978), 21-33.
10. Spanjers, H. and Vanrolleghem, P.A., Respirometry as a tool for rapid characterization of wastewater and activated sludge, *Water Sci. Technol.*, 31(2) (1995), 105 - 114.
11. Walter, E., Identifiability of state space models, Springer, Berlin, 1982.