



Reaction invariant-based reduction of the activated sludge model ASM1 for batch applications



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ABSTRACT

In any system, there are some properties, quantities or relationships that remain unchanged despite the applied transformations (system invariants). For a batch reaction system with n linearly independent reactions and m components ($n < m$) there exist linear combinations of the concentrations that are unaffected by the reaction progress, i.e. so-called reaction invariants. The reaction invariant concept can be used to reduce the number of ordinary differential equations (ODEs) involved in batch bioreactor models. In this paper, a systematic methodology of model reduction based on this concept is applied to batch activated sludge processes described by the Activated Sludge Model No. 1 (ASM1) for carbon and nitrogen removal. The objective of the model reduction is to describe the exact dynamics of the states predicted by the original model with a lower number of ODEs. This leads to a reduction of the numerical complexity as nonlinear ODEs are replaced by linear algebraic relationships predicting the exact dynamics of the original model.

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1. Introduction

In general, the dynamics of biochemical processes mediated by pure or mixed microbial cultures is an issue of main concern from both a theoretical and applied point of view in the biotechnological and environment-related fields. The activated sludge processes form a clear example; they are widely used for removal of organic carbonaceous matter (carbon, C) and nutrients (nitrogen, N, and phosphorus, P) from municipal and industrial wastewater streams. In the mixed microbial consortia that constitute the activated sludge, the interactions established among the different microbial populations are quite complex. For that reason, structured and non-structured mathematical models with different degree of complexity and detail have been developed to represent such intricate microbiological interactions, and then, to predict the

process performance under the imposed operating conditions. In this regard, a task group created under the umbrella of the International Water Association (IWA) has made significant efforts to develop mathematical models of the activated sludge process, which are widely known as the Activated Sludge Model (ASM) family: ASM1 [1], ASM2 [2], ASM2d [3] and ASM3 [4]. These models are intended to condensate the present understanding of the relevant biological and biochemical phenomena taking place in such complex processes. This model family is considered to be the state-of-the-art of activated sludge models for research, training and teaching purposes, albeit in practice they have to be calibrated, adapted or adjusted to the particular case under study.

However, it is well known that the use of complex/large highly nonlinear dynamic models is sometimes inadvisable when they are included into optimization routines or approaches; indeed, difficulties may arise in determining a large number of parameters and/or in manipulating a large number of differential equations for optimization purposes. In such applications, simpler and small or medium-size models are desired which should be sufficiently detailed to adequately describe the variables dictating the main process dynamics.

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In the modeling and simulation field, the terms “model reduction”, “model order reduction”, “model simplification” and so on, may in general sound somewhat ambiguous or unspecific; the definition of these terms depends mainly on the context and application field in which they are used. In this paper, the term “model reduction” should be understood as an analytical technique to represent a dynamic model of a system, named the “original” model, with a lower number of differential equations to reduce its numerical complexity but keeping its dynamic behavior. The “reduced” model should not be understood as a “simplification” of the original model in terms of the degree of detail for describing the involved physical or (bio)chemical phenomena.

In general, the complexity of reaction kinetic models depends on the number of components and chemical and/or biochemical reactions, and mainly on the nature of the mathematical expressions that describe the process rates.

The model that describes the dynamics of the reactor system studied in this work consists on nonlinear ordinary differential equations (ODEs) representing the mass balances of the chemical species and microbiological species (biomass). As isothermal conditions are often assumed, the energy balance can in that case be ignored. This assumption–isothermal condition–is generally accepted in activate sludge system modeling, although temperature corrections are possible using Arrhenius-type equations (temperature corrections were given with the ASM2d model and ASM1 was provided with a set of parameters for two different temperatures).

In any system of physical, chemical or biological nature, or a combination of them, there are some properties, elements, quantities or relationships of the system that remain unchanged despite the transformations applied to it. These properties, elements, amounts or relationships are called invariants of the system.

A pioneering work on the fundamental principles on the theory of invariants was presented by Glenn in 1915 [5], which has been recently reprinted [6]. Because of the property of the reaction invariants of being independent of the reaction progress, the concept of reaction invariants has been successfully used for design, control, and analysis of processes. Reaction invariants were first used for studying the dynamics of process systems by Asbjørnsen and co-workers in several papers on reactor dynamics and control [7–9], where systematic methods were proposed to separate the state space of a reacting system into invariants and variants using linear algebra to perform the transformations, allowing to handle large chemical systems on computers. Fjeld et al. [9] have used reaction invariants to reduce the dimensionality of the system of differential equations describing the dynamics of processes in continuous stirred tank reactors, and highlighted the importance of using reaction invariants for the analysis of eigenvectors, state observability and controllability of the continuous stirred tank reactor. Srinivasan et al. [10] extended this methodology to include flow invariants for such systems using nonlinear transformations. Gadewar et al. [11] proposed a framework for automating the determination of mole balances around and between plants in complexes –such as petrochemical, pharmaceutical, specialty chemical, and pesticide manufacturing complexes– represented as a state-task network, where the reaction invariants are used for formulating the component balances. Mole balances for mixing and splitting of component flows are identified automatically, which provides the structure of the coupling between plants and a systematic means to identify options to make or buy intermediates, and thus helping to determine the number of degrees of freedom for the synthesis of the process. Waller and Mäkilä [12] recognized that reaction invariants have their origins in the fundamental laws of conservation. They illustrated the utilization of the concepts of

reaction invariants and variants in chemical reactor modeling, simulation and control, through the simulation of an industrial cement kiln described by a number of partial differential equations, and showed that the computational burden can be significantly reduced through use of reaction invariants and variants. They extended the concept to include enthalpy as a reaction invariant for liquid systems. They showed that both the design and implementation of the control of acid-base systems can be significantly simplified if the synthesis and implementation is limited to the space of the variants only, which contains the possible instability and the possible nonlinearities caused by the chemical reactions. Thus, by use of the chemical reaction invariants the state space of main concern in control can be considerably reduced facilitating the design, implementation, and operation of control systems. In addition, they demonstrated the use of reaction invariants to control pH when the equilibrium reactions are assumed to be very fast. For model reduction of reactive distillation processes with simultaneous phase and reaction equilibrium, Barbosa and Doherty [13,14], Ung and Doherty [15–17], and Gadewar et al. [18] have developed and applied a method for determining the reaction invariants for complex chemistries using linear transformations through the introduction of a set of transformed composition variables for the representation of reactive-phase diagrams, with the purpose of designing and studying the steady state behavior of reactive distillation systems. The reaction invariants are used to transform the state of a reactive distillation to the similar states of a non-reactive system. Because the balances based on reaction invariants do not have kinetic reaction rates, it allows simplifying feasibility and column sequencing strategy for equilibrium reactive distillation systems. The reaction invariants have also been used for analyzing the dynamics of reactive separation processes. Grüner et al. [19] have shown that the dynamic behavior of combined reaction-separation processes with fast chemical reactions is equivalent to the dynamic behavior of the corresponding nonreactive problem in a reduced set of transformed concentration variables –the reaction invariants–; they showed applications for reactive distillation processes, fixed bed as well as moving-bed chromatographic reactors, and membrane reactors. Vu et al. [20] reported applications of this concept for analyzing the dynamics of chromatographic reactors, and Huang et al. [21] for analyzing the dynamics of reactive pervaporation processes. Flockerzi et al. [22] provided a systematic procedure for the computation of reaction invariant compositions, which are obtained, in this case, from a nonlinear transformation of the original composition variables. The transformation requires the choice of a suitable set of reference components; they proved that such a set always exists. Aggarwal et al. [23] proposed a modeling framework for stable simulation of multi-phase reactors operating at thermodynamic equilibrium using the concept of reaction invariants – which they named invariant inventories or simply invariants – to reduce the order of the dynamic model, which can be used to determine system characteristics, explore parameter sensitivity, and test control system strategies at a low computational burden. They showed that the feedback control approach based on the overall inventories of the system (reaction invariants) can be effectively used for improved performance of the vapor recovery reactor used in the carbothermic aluminum reduction and of the gasification reactor used in an integrated gasification combined cycle (IGCC) power plant. Recently, Srinivasan et al. [24] and Rodrigues et al. [25] have addressed the computation of variant and invariant quantities for open homogeneous and heterogeneous reaction systems. They extended the reaction variants/invariant concept used in the context of batch processes to consider the effects of inlet/outlet flows, mass transfer between phases, and convection and diffusion. They showed that each extent describes uniquely and completely the progress of the

corresponding process, and that the defined invariants are true invariants that are identically equal to zero and can be discarded from the dynamic model. These ideas are intended to improve the analysis, control, estimation, and optimization of reaction systems. Stamatelatos et al. [26] proposed a methodology for reducing dynamic models for multi-step biochemical reaction schemes in continuous stirred tank reactors. It is based on an invariant manifold formulation of the model reduction problem that projects the reactor dynamics on the slow motion invariant manifold, which is computed by using reaction invariants for describing the dynamics, and then, the invariance equation is solved by means of singular perturbation or series solution methods. They applied the methodology for model reduction of the anaerobic digestion process to eliminate the fast dynamics of the acidogenesis step. Cruz Bournazou et al. [27] performed model reductions of the ASM3 model extended for two-step nitrification–denitrification for describing the activated sludge process with nitrate bypass nitrification–denitrification. They applied the concept of reaction invariants as one of the approaches used to progressively reduce the fifteen-state variable model to a five-state variable model under appropriate assumptions and considerations in a sequencing batch reactor.

The objective of this work is to reduce the number of states described by ODEs of a discontinuous (batch) bioreactor, where the microbiological consortia and their multi-step biochemical conversion scheme for C and N removal from municipal and industrial wastewaters is represented by the Activated Sludge Model No 1 (ASM1) [1]. The goal is to decrease the degree of numerical complexity but predicting the exact dynamic behavior of the original model for further applications in dynamic optimization of wastewater treatment systems. A systematic methodology is applied for the reduction of models in batch-type reactor configurations. The methodology is based on the concept of reaction invariants. It should be emphasized that the focus is not on reducing the required computational time (e.g. [28]), but on reducing the number of ODEs to describe the states of the system while keeping its exact dynamics.

The paper is organized as follows. The applied general methodology is presented in Section 2. The stoichiometry and the process kinetics of the ASM1 model are summarized in Section 3. In Section 4, the theory of reaction invariants is applied to a simple case as an illustrative example, where only one reaction invariant is obtained (case study 1). Afterwards, two more realistic case studies are considered. In the case study 2, a reduction of an aerated (aerobic) batch bioreactor model is performed by proposing three reaction invariants; in the case study 3, a reduction of a non-aerated (anoxic) batch bioreactor model is accomplished by considering five reaction invariants (i.e. the maximum number of reaction invariants possible for the ASM1 model). Finally, a discussion of results and conclusions is included in Section 5.

2. Methodology

For a given closed reaction system (i.e. without incoming and outgoing mass flows), let n be the scalar representing the (maximum) number of linearly independent (LI) reactions, and m the number of system components. Then, there are $(m-n)$ linear combinations of the concentrations of such components that are unaffected by the reaction rates and, therefore, independent of the progress of the chemical reactions taking place. These linear combinations are the *reaction invariants*; these invariants “capture” the stoichiometric relationships among the components involved in the reactions, which are unaffected by the reaction rates [26]. It should be noted that closed systems are being considered in this work. For systems with convective mass flows, the system invariants are obtained by a different methodology since they

depend on the flow rate [10,26]. This issue will be addressed in a later work.

Let $\mathbf{C} \in R^{m \times n}$ be the matrix of stoichiometric coefficients of the system of rank n ($\text{rk}(\mathbf{C}) = n$). The m rows and n columns represent the m components and the n reactions, respectively. If $\mathbf{x} \in R^m$ is the vector of states, $\dot{\mathbf{x}}$ the vector of time derivatives of \mathbf{x} and $\mathbf{r}(\mathbf{x}) \in R^n$ the vector of reaction rates, then the system dynamics in a batch reactor (no inflow and outflow) is described by:

$$\dot{\mathbf{x}} = \mathbf{C} \cdot \mathbf{r}(\mathbf{x}) \quad (1)$$

The vector $\boldsymbol{\varsigma} \in R^{m-n}$ of reaction invariants is obtained by applying the following methodology. A matrix $\mathbf{A} \in R^{(m-n) \times m}$ has to be found that meets the condition:

$$\mathbf{A} \cdot \mathbf{C} = \mathbf{0} \quad (2)$$

and the rank of \mathbf{A} is $(m-n)$, i.e. all its rows (row vectors) must be linearly independent LI:

$$\text{rk}(\mathbf{A}) = m - n \quad (3)$$

Let a_{ij} be a generic element of the matrix \mathbf{A} . The matrix product (2) determines the following homogeneous linear system of $(m-n) \cdot n$ equations with $(m-n) \cdot m$ unknowns a_{ij} :

$$\sum_{j=1}^m a_{ij} \cdot c_{jk} = 0; k = 1, \dots, n; i = 1, \dots, m - n \quad (4)$$

The linear equation system (4) is an underdetermined system. For it to have one unique non-trivial solution (i.e. a consistent system with one solution or independent system), it is necessary to choose $[(m-n) \cdot m - (m-n) \cdot n] = (m-n)^2$ variables a_{ij} (called the set $\boldsymbol{\alpha}$). Let $\mathbf{P} \in R^{(m-n) \times n \times (m-n)^m}$ be the coefficient matrix of the underdetermined linear equation system (4). By applying the Gauss-Jordan elimination (G-J) method with partial pivoting to the matrix \mathbf{P} , the diagonalized matrix $\mathbf{P}_{\text{trans}} \in R^{(m-n) \times n \times (m-n)^m}$ is obtained and, consequently, the set $\boldsymbol{\alpha}$. Afterwards, each a_{ij} of $\boldsymbol{\alpha}$ has to be assigned a scalar value h_{ij} (called the set $\boldsymbol{\beta}$). However, not any set $\boldsymbol{\beta}$ leads to $(m-n)$ LI rows (second condition to be met by the matrix \mathbf{A} according to Eq. (3)). To find a set $\boldsymbol{\beta}$ that meets this condition, an *ad hoc* algorithm has been developed in Matlab, which is provided as Supplementary material associated with this article.

The linear system Eq. (4) extended with these linear assignments results in the following linear equation system Eq. (5):

$$\mathbf{Q} \cdot \mathbf{w} = \mathbf{b} \quad (5)$$

$\mathbf{Q} \in R^{(m-n)m \times (m-n)^m}$ is the coefficient matrix of the linear system obtained by extending \mathbf{P} with the variables a_{ij} that were assigned, which must not be singular ($\det \mathbf{Q} \neq \mathbf{0}$); $\mathbf{b} \in R^{(m-n)^m}$ is the vector of independent terms formed by the vector null $\mathbf{0}$ of the homogeneous system Eq. (4) and the vector $\boldsymbol{\beta}$ of scalars h_{ij} :

$$\mathbf{b}^T = (\mathbf{0}\boldsymbol{\beta}) \quad (6)$$

$\mathbf{w} \in R^{(m-n)^m}$ is the vector of elements a_{ij} of matrix \mathbf{A} , i.e. the vector of unknowns of the linear system Eq. (4):

$$\mathbf{w}^T = (a_{1,1} \dots a_{1,m} a_{2,1} \dots a_{2,m} a_{m-n,1} \dots a_{m-n,m}) \quad (7)$$

The solution of the equation system Eq. (5) is then:

$$\mathbf{w} = \mathbf{Q}^{-1} \cdot \mathbf{b} \quad (8)$$

Thus, the desired matrix \mathbf{A} can be obtained:

$$\mathbf{w}^T = (a_{1,1} \dots a_{1,m} a_{2,1} \dots a_{2,m} a_{m-n,1} \dots a_{m-n,m}) \rightarrow \mathbf{A} = \begin{pmatrix} a_{1,1} & \dots & a_{1,m} \\ \vdots & \ddots & \vdots \\ a_{m-n,1} & \dots & a_{m-n,m} \end{pmatrix} \quad (9)$$

Call $\varsigma \in R^{(m-n)}$ the vector of reaction invariants and ς_i represents each of its elements. Reaction invariants are the linear combinations obtained from the following linear equation system:

$$\mathbf{s} = \mathbf{A} \cdot \mathbf{x} \tag{10}$$

For batch systems, these linear combinations remain constant before, during and after the reaction [29]. Based on this property, and letting \mathbf{x}^{in} be the vector of initial conditions (at $t=0$) of the state vector \mathbf{x} , the (constant) value of each invariant ς_i is obtained by replacing in Eq. (10) the initial conditions \mathbf{x}^{in} :

$$\varsigma_i = \sum_{j=1}^m a_{ij} \cdot x_j = \sum_{j=1}^m a_{ij} \cdot x_j^{in}; i = 1, \dots, m - n \tag{11}$$

Since the row vectors of matrix \mathbf{A} must be LI, so will the resulting invariants vector ς . The model reduction order σ is equal to the dimension of vector ς , in this case $(m-n)$: $\sigma = rk(\varsigma) = (m-n)$. Finally, the algebraic expression corresponding to a given state variable x_k can be obtained from a linear combination ς_i as:

$$x_{j=k} = \frac{1}{a_{ik}} \cdot \left(\varsigma_i - \sum_{\substack{j=1 \\ j \neq k}}^m a_{ij} \cdot x_j \right); i = 1, \dots, m - n \tag{12}$$

In this way, by applying the theory of reaction invariants, the reduced model is formed by $(m-n)$ state variables expressed algebraically and n state variables expressed in the (original) differential form.

3. Activated sludge model No 1 (ASM1)

The complete ASM1 model is represented by the Petersen matrix (Table 1), which helps in identifying the overall reaction rate of each model component. This matrix notation allows a compact and visually appealing description of complex mathematical models [30–32]. As a detailed description of the ASM1 model can be found in [1] and [31], only a minimum of information about the examined model is provided here. The activated sludge model ASM1 describes the oxidation of carbonaceous organic matter, nitrification and denitrification. The model consists of $n=8$ processes, $m=13$ components and 19 parameters (5 stoichiometric and 14 kinetic parameters). Regarding the model components, 7 are soluble (S) and 6 are particulate (X) compounds. Seven of the 13 components are carbonaceous: 2 soluble (inert soluble compounds S_I and rapidly biodegradable substrate S_S) and 5 particulate compounds (inert X_I , slowly biodegradable substrate X_S , heterotrophs X_{BH} , autotrophs X_{BA} and products arising from biomass decay X_P), whose concentrations are expressed in terms of chemical oxygen demand (COD). The carbonaceous matter is divided into biodegradable COD (S_S and X_S), non-biodegradable COD (S_I , X_I and X_P) and active biomass (X_{BH} and X_{BA}). Four of the 13 components are nitrogenous compounds: 3 soluble (ammonium + ammonia nitrogen, S_{NH} , nitrate + nitrite nitrogen, S_{NO} , and biodegradable organic nitrogen, S_{ND}) and 1 particulate compound (biodegradable organic nitrogen X_{ND}), expressed in $g N m^{-3}$ units. The biodegradable nitrogen consists of a soluble fraction (S_{ND}) and a particulate fraction (X_{ND}). The remaining 2 model components

Table 1
Petersen matrix for the ASM1 [31]. Process kinetics and stoichiometry for carbon oxidation, nitrification and denitrification.

Component → Process j	i	1	2	3	4	5	6	7	8	9	10	11	12	13	Process rate ρ_j [ML ⁻³ T ⁻¹]	
		S_j	S_S	X_I	X_S	X_{BH}	X_{BA}	X_P	S_O	S_{NO}	S_{NH}	S_{ND}	X_{ND}	S_{ALK}		
1 Aerobic growth of heterotrophs			$\frac{1}{Y_H}$			1			$-\frac{1-Y_H}{Y_H}$						$\hat{\mu}_H \frac{S_S}{K_S + S_S} \frac{S_O}{K_{O,H} + S_O} X_{BH}$	
2 Anoxic growth of heterotrophs			$\frac{1}{Y_H}$			1			$-\frac{1-Y_H}{2.86 Y_H}$						$\hat{\mu}_H \frac{S_S}{K_S + S_S} \frac{K_{O,H}}{K_{O,H} + S_O} \frac{K_{O,A}}{K_{O,H} + S_O} \eta_H X_{BH}$	
3 Aerobic growth of autotrophs							1		$\frac{4.57-Y_A}{Y_A}$	$\frac{1}{Y_A}$					$\hat{\mu}_A \frac{S_{NH}}{K_{NH} + S_{NH}} \frac{S_O}{K_{O,A} + S_O} X_{BA}$	
4 Decay of X_{BH}					$1-f_P$	-1		f_P							$b_H X_{BH}$	
5 Decay of X_{BA}					$1-f_P$		-1	f_P							$b_A X_{BA}$	
6 Amonif. of S_{ND}												1	-1	1/14	$k_e S_{ND} X_{BH}$	
7 Hydrolysis of entrapped organics			1		-1										$k_H \frac{X_S}{K_X + X_S} \frac{X_{BH}}{K_{O,H} + S_O} \left(\frac{S_O}{K_{O,H} + S_O} + \eta_h \frac{K_{O,H}}{K_{O,H} + S_O} \frac{S_{NO}}{K_{NO} + S_{NO}} \right) X_{BH}$	
8 Hydrolysis of X_{ND}													1	-1	$\rho_7 \frac{X_{ND}}{X_S}$	
<i>Stoichiom. param.:</i> Heterotrop. yield Y_H Autotrop. yield Y_A Biomass fraction to particulates f_P Biomass N/COD i_{XB} N/COD in products from biomass i_{XP}		Sol. inert org. matter [M(COD)L ⁻³] Readily biod. substrate [M(COD)L ⁻³] Partic. inert org. matter [M(COD)L ⁻³] Slowly biod. substrate [M(COD)L ⁻³] Active heterotrophs [M(COD)L ⁻³] Active autotrophs [M(COD)L ⁻³] Partic. from biomass decay [M(COD)L ⁻³] Oxygen (negative COD) [M(-COD)L ⁻³] Nitrate and nitrite nitrogen [M(N)L ⁻³] NH_4^+ + NH_3 +N [M(N)L ⁻³] Sol. biod. org. N [M(N)L ⁻³] Particulate biod. org. N [M(N)L ⁻³] Alkalinity [Mol L ⁻³]														<i>Kinetics param.:</i> Heterotrophic growth and decay: $\hat{\mu}_H \cdot K_S \cdot K_{O,H} \cdot K_{O,A} \cdot b_H$ Autotrophic growth and decay: $\hat{\mu}_A \cdot K_{NH} \cdot K_{O,A} \cdot b_A$ Factor of anox. growth of X_{BH} : η_H Ammonification: k_e Hydrolysis: k_H, K_X Factor for anoxic hydrolysis: η_h

Observed conversion rates [ML⁻³T⁻¹]: $r_i = \sum_j Y_{ij} \rho_j$

are dissolved oxygen (S_O) and alkalinity (S_{ALK}), expressed in $g\ O_2\ m^{-3}$ and mole $CaCO_3\ m^{-3}$, respectively.

The ASM1 model considers four types of processes: growth and decay of X_{BH} and X_{BA} , ammonification of S_{ND} , hydrolysis of X_S , and hydrolysis of X_{ND} (Table 1). The use of the Petersen matrix to formulate the differential equation describing the dynamics of the model components is explained in [30] and [33]. The overall component conversion rates \mathbf{r} can be calculated as the sum of conversion rates of components involved in each process:

$$r_i = \sum_j v_{ij} \rho_j \quad (13)$$

For example, writing \mathbf{r} for the active heterotrophic biomass is done as follows: component $i=5$, process $j=1, 2, 4$, and $\mathbf{v}_{ij}=1, 1, -1$. Then,

$$\begin{aligned} r_5 &= 1 \cdot \rho_1 + 1 \cdot \rho_2 + (-1) \cdot \rho_4 \\ \rho_1 &= \mu_h \cdot \frac{S_S}{K_S + S_S} \cdot \frac{S_O}{K_{OH} + S_O} \cdot X_{BH} \\ \rho_2 &= \mu_h \cdot \frac{S_S}{K_S + S_S} \cdot \frac{K_{OH}}{K_{OH} + S_O} \cdot \frac{S_{NO}}{K_{NO} + S_{NO}} \cdot \eta_g \cdot X_{BH} \\ \rho_4 &= b_H \cdot X_{BH} \end{aligned} \quad (14)$$

Finally, the calculated overall component conversion rates can be coupled with appropriate mass balance equations to obtain the ODE for this component; for instance, for active heterotrophic biomass in batch systems, the resulting ODE is the following:

$$\begin{aligned} \frac{dX_{BH}}{dt} &= 1 \cdot \mu_h \cdot \frac{S_S}{K_S + S_S} \cdot \frac{S_O}{K_{OH} + S_O} \cdot X_{BH} \\ &+ 1 \cdot \mu_h \cdot \frac{S_S}{K_S + S_S} \cdot \frac{K_{OH}}{K_{OH} + S_O} \cdot \frac{S_{NO}}{K_{NO} + S_{NO}} \cdot \eta_g \cdot X_{BH} - b_H \cdot X_{BH} \end{aligned} \quad (15)$$

4. Results and discussion

The described methodology is applied to three case studies, where the biological conversion scheme, represented by the ASM1 model for C and N removal, in batch reactors is reduced. The case study 1 (CS1) is a simple example where a model reduction by 1 order (i.e. 1 reaction invariant) is accomplished to illustrate the methodology.

In the case studies 2 (CS2) and 3 (CS3), two more realistic situations are presented. In CS2, an aerobic batch reactor is considered where a reduction by 3 orders (3 reaction invariants) is performed. In CS3, a reduction by 5 orders (5 reaction invariants) is conducted for an anoxic batch bioreactor.

Batch bioreactor models represented by the original ASM1 model and its reductions were simulated in the general PROcess Modelling Systems (gPROMS) environment [34–36] for results comparison.

4.1. Case study 1 (CS1): 1 reaction invariant

Since the ASM1 model consists of 8 independent processes (reactions), it is necessary to consider only 9 of the 13 model components. Therefore, 4 components have to be excluded from the reduction procedure. The two inert components (S_i and X_i), alkalinity (S_{ALK}) and oxygen (S_O) were excluded. In this case, the stoichiometric coefficient matrix $\mathbf{C} \in R^{(9 \times 8)}$ is of rank 8, which is obtained by eliminating the rows corresponding to the model components that are not incorporated into the reduction procedure from the transpose of the Petersen matrix of the ASM1 model

(Table 1).

$$\mathbf{C} = \begin{pmatrix} \frac{1}{y_H} & \frac{1}{y_H} & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & \frac{1-y_H}{2.86 \cdot y_H} & \frac{1}{y_A} & 0 & 0 & 0 & 0 & 0 \\ -i_{xb} & -i_{xb} & -i_{xb} - \frac{1}{y_A} & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 1 \\ 0 & 0 & 0 & 1-f_p & 1-f_p & 0 & -1 & 0 \\ 1 & 1 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & f_p & f_p & 0 & 0 & 0 \\ 0 & 0 & 0 & i_{xb} - f_p \cdot i_{xp} & i_{xb} - f_p \cdot i_{xp} & 0 & 0 & -1 \end{pmatrix} \quad (16)$$

The desired matrix \mathbf{A} has the dimension $(9-8) \times 9$:

$$\mathbf{A} = (a_{1,1} \ a_{1,2} \ a_{1,3} \ a_{1,4} \ a_{1,5} \ a_{1,6} \ a_{1,7} \ a_{1,8} \ a_{1,9}) \quad (17)$$

Therefore, the system of 8 equations with 9 unknowns that results according to Eq. (2) is:

$$\begin{cases} a_{1,1} \cdot \left(\frac{1}{y_H}\right) + a_{1,3} \cdot (-i_{xb}) + a_{1,6} = 0 \\ a_{1,1} \cdot \left(\frac{1}{y_H}\right) + a_{1,2} \cdot \left(\frac{1-y_H}{2.86 \cdot y_H}\right) + a_{1,3} \cdot (-i_{xb}) + a_{1,6} = 0 \\ a_{1,2} \cdot \left(\frac{1}{y_A}\right) + a_{1,3} \cdot \left(-i_{xb} - \frac{1}{y_A}\right) + a_{1,7} = 0 \\ a_{1,5} \cdot (1-f_p) + a_{1,6} \cdot (-1) + a_{1,8} \cdot f_p + a_{1,9} \cdot (i_{xb} - f_p \cdot i_{xp}) = 0 \\ a_{1,5} \cdot (1-f_p) + a_{1,7} \cdot (-1) + a_{1,8} \cdot f_p + a_{1,9} \cdot (i_{xb} - f_p \cdot i_{xp}) = 0 \\ a_{1,3} + a_{1,4} \cdot (-1) = 0 \\ a_{1,1} + a_{1,5} \cdot (-1) = 0 \\ a_{1,4} + a_{1,9} \cdot (-1) = 0 \end{cases} \quad (18)$$

In order to determine the free variable a_{ij} of the under-determined linear system Eq. (18), the G-J method with partial pivoting is applied using the “rref” function of Matlab. It converts the coefficient matrix \mathbf{P} of dimension 8×9 into a reduced echelon form \mathbf{P}_{transf} by transformations, with as many leading “1” values on the diagonal as possible. The free variables are those that are not diagonalized, i.e., they do not contain “1” in the main diagonal of the transformed matrix. The following transformed matrix \mathbf{P}_{transf} is obtained, resulting in $a_{1,9}$ as the free variable:

$$\mathbf{P}_{transf} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -2.79 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & -2.79 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & -4.25 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & -4.25 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -20.04 \end{pmatrix} \quad (19)$$

With this procedure, the equivalent linear system Eq. (20) is obtained:

$$\begin{cases} a_{1,1} - 2.79 \cdot a_{1,9} = 0 \\ a_{1,2} = 0 \\ a_{1,3} - 1 \cdot a_{1,9} = 0 \\ a_{1,4} - 1 \cdot a_{1,9} = 0 \\ a_{1,5} - 2.79 \cdot a_{1,9} = 0 \\ a_{1,6} - 4.25 \cdot a_{1,9} = 0 \\ a_{1,7} - 4.25 \cdot a_{1,9} = 0 \\ a_{1,8} - 20.04 \cdot a_{1,9} = 0 \end{cases} \quad (20)$$

The following assignment is then added to the linear system Eq. (18) as the 9th equation:

$$a_{1,9} = 1 \quad (21)$$

The coefficient matrix \mathbf{Q} of the resulting linear system is given by Eq. (22), in which the assignment Eq. (21) is represented by the

last row:

$$\mathbf{Q} = \begin{pmatrix} \frac{1}{y_H} & 0 & -i_{xb} & 0 & 0 & 1 & 0 & 0 & 0 \\ \frac{1}{y_H} & \frac{1-y_H}{2.86 \cdot y_H} & -i_{xb} & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & \frac{1}{y_A} & -i_{xb} - \frac{1}{y_A} & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1-f_p & -1 & 0 & f_p & i_{xb} - f_p \cdot i_{xp} \\ 0 & 0 & 0 & 0 & 1-f_p & 0 & -1 & f_p & i_{xb} - f_p \cdot i_{xp} \\ 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \quad (22)$$

According to Eq. (6), in this case, the vector **b** of independent terms is:

$$\mathbf{b}^T = (\mathbf{0}\boldsymbol{\beta}) = (000000001) \quad (23)$$

The vector **w** and, consequently, the elements a_{ij} of the desired matrix **A** (Eq. (9)) are obtained from Eq. (8):

$$\mathbf{w}^T = \mathbf{A} = (2.79 \ 0 \ 1 \ 1 \ 2.79 \ 4.25 \ 4.25 \ 20.04 \ 1) \quad (24)$$

If the vector **x** of states is given by Eq. (25) and with the vector \mathbf{x}^{in} of initial conditions given by Eq. (26), the system reaction invariant $\zeta_{a1,9}$ is obtained from Eq. (11).

$$\mathbf{x} = (S_S S_{NO} S_{NH} S_{ND} X_S X_{BH} X_{BA} X_P X_{ND}) \quad (25)$$

$$\mathbf{x}^{in} = (40.23 \ 8.55 \ 19.07 \ 4.19 \ 148.65 \ 2305.03 \ 126.85 \ 338.89 \ 8.67) \quad (26)$$

$$\zeta_{a1,9} = 2.79 \cdot (S_S + X_S) + (S_{NH} + S_{ND} + X_{ND}) + 4.25 \cdot (X_{BH} + X_{BA}) + 20.04 \cdot X_P = 17677.73 \quad (27)$$

Any variable can be isolated from Eq. (27) to be expressed algebraically. In this case, the rapidly degradable substrate concentration S_S is selected for reducing the model, which implies replacing the ODE Eq. (28) in the original model, which represents the mass balance for the component S_S , by the linear algebraic equation Eq. (29) obtained from the reaction invariant given by Eq. (27). Note that the dynamics of the other states of the reduced model is still described by the original ODEs.

$$\frac{dS_S}{dt} = \frac{(-1)}{y_H} \mu_h \frac{S_S}{K_S + S_S} \frac{S_O}{K_{OH} + S_O} X_{BH} + \frac{(-1)}{y_H} \mu_h \frac{S_S}{K_S + S_S} \frac{K_{OH}}{K_{OH} + S_O} \frac{S_{NO}}{K_{NO} + S_{NO}} \eta_g X_{BH} + K_H \frac{x_s/x_{BH}}{K_X + x_s/x_{BH}} \left(\frac{S_O}{K_{OH} + S_O} + \eta_h \frac{K_{OH}}{K_{OH} + S_O} \frac{S_{NO}}{K_{NO} + S_{NO}} \right) X_{BH} \quad (28)$$

$$S_S = 6336.10 - 0.36 \cdot (S_{NH} + S_{ND} + X_{ND}) - X_S - 1.52 \cdot (X_{BH} + X_{BA}) - 7.18 \cdot X_P \quad (29)$$

The dynamics of the component S_S obtained by simulating an aerated phase followed by a non-aerated phase (60% and 40% of the total time horizon, respectively) of a batch reactor using the original model and the resulting reduced model are compared in Fig. 1. The initial conditions (at $t=0$) for the variables included into the reduction procedure (Eq. (25)) are given by Eq. (26) and for the variables that were not included are: $S_O^{in} = 0 \text{ g O}_2 \text{ m}^{-3}$, $X_i^{in} = 980.32 \text{ g COD m}^{-3}$, $S_i^{in} = 30 \text{ g COD m}^{-3}$ and $S_{ALK}^{in} = 5.49 \text{ mol CaCO}_3 \text{ m}^{-3}$. The $k_{i,a}$ values of 240 and 0 d^{-1} for the aerobic and anoxic phases, respectively, were set. The default parameter values of the ASM1 model [31] were used. Both models predict exactly the same dynamic behavior. The concentration S_S intervenes in the kinetic expressions of several other reactions forming the model.

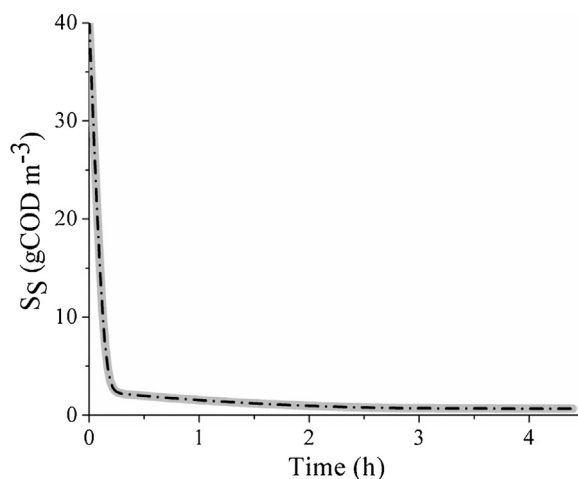


Fig. 1. Dynamics of the component S_S predicted by the original model (solid line) and the reduced model (dash-dotted line) for CS1.

As expected, comparing the dynamics for each component predicted by both models, there is total agreement between them (results not shown) thereby demonstrating the validity of the approach.

It should be noted that the application of the G-J method determines that the variable $a_{1,2}$ can only be assigned to 0. Since $a_{1,2}$ is the element of matrix **A** related to nitrate (S_{NO}), it is concluded that it is not possible to obtain its concentration as an algebraic variable from the resulting reaction invariant expressions.

By inspecting the ASM1 process rate expressions (Table 1) and the component mass balance equations, it can be observed, for instance, that if the state X_{ND} (component #12 in Table 1) is expressed as an algebraic variable in CS1 using the invariant expression Eq. (27), the stoichiometric coefficient i_{xp} (mass N/mass COD in products from biomass) will not be present in the resulting reduced model. However, it is also important to emphasize that all the stoichiometric coefficients of the original model must be known values when starting the reduction procedure.

4.2. Case study 2 (CS2): 3 reaction invariants

In this case study, 3 reaction invariants are obtained; consequently, 3 states of the system can be represented by 3 linear algebraic relationships. This reduction is applied to the aerobic phase of the reaction stage of a batch activated sludge process. Unlike CS1, the inert soluble component S_i and the alkalinity S_{ALK} are now incorporated into the reduction procedure. Instead, oxygen (S_O) and inert particulate material (X_i) are excluded from it. In this case, the system's stoichiometric coefficients matrix $\mathbf{C} \in \mathbb{R}^{(11 \times 8)}$ is of rank 8, with 11 components and 8 reactions. The matrix **A** that is to be found then has the dimension $(11 - 8) \times 11$:

$$\mathbf{A} = \begin{pmatrix} a_{1,1} & \dots & a_{1,11} \\ \vdots & \ddots & \vdots \\ a_{3,1} & \dots & a_{3,11} \end{pmatrix} \quad (30)$$

The generated homogeneous linear system ($\mathbf{A} \cdot \mathbf{C} = \mathbf{0}$ (2)) consists of 24 equations and 33 unknowns; then, 9 free variables a_{ij} (set $\boldsymbol{\alpha}$) should be selected and assigned values h_{ij} , where h_{ij} values are either 0 or 1 (set $\boldsymbol{\beta}$), thereby generating a combinatorial problem. The set $\boldsymbol{\alpha}$ of free variables a_{ij} is obtained by applying the G-J method with partial pivoting to the matrix **P** resulting in a

non-singular matrix \mathbf{Q} . The set β is obtained by applying the *ad hoc* algorithm described in the Supplementary material associated with this article. Now, it was found that the final expressions of the reaction invariants ς_i are sensitive to the relative number of “0” and “1” elements of the set β , and that it is not possible to obtain solutions with a certain number of “0” values and “1” values in the set β . It was found that if one, two, eight or nine of the nine elements h_{ij} of the set β are “1”, it is not possible to find a matrix \mathbf{A} with row vectors \mathbf{L} . So, the algorithm provides solutions with three to seven times the value “1” in the set β , randomly distributed among the free variables a_{ij} to be assigned. There is a direct relation between the number of times the value “1” is assigned among the free variables a_{ij} and the number of terms present in the resulting algebraic equations of the reaction invariants. The lower the number of times the value “1” has been used, the shorter the reaction invariant expressions (without accuracy loss in the predictions), but the smaller the number of states that can be expressed as algebraic variables. The set α obtained by the G-J method and one of the sets β with three “1” values generated by the *ad hoc* algorithm are:

$$\alpha = (a_{1,1} a_{1,6} a_{1,11} a_{2,1} a_{2,6} a_{2,11} a_{3,1} a_{3,6} a_{3,11})$$

$$\beta = (0 \ 0 \ 1 \ 1 \ 0 \ 0 \ 0 \ 1 \ 0)$$

Thus, the coefficient matrix \mathbf{Q} of dimension 33×33 is obtained (not shown), whose last 9 rows correspond to the previous assignments, and the vector \mathbf{b} formed by 24 null elements and the 9 elements of the set β : $\mathbf{b}^T = (\mathbf{0} \ \beta)$.

The vector \mathbf{w} and, consequently, the matrix \mathbf{A} of rank 3 to be found are obtained from Eqs. (8) and (9), respectively:

$$\mathbf{A} = \begin{pmatrix} 0 & 2.79 & 0 & 1 & 1 & 0 & 2.79 & 4.25 & 4.25 & 20.04 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0.0714 & -0.0714 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (31)$$

If the state vector \mathbf{x} and the initial condition vector \mathbf{x}^{in} are the following:

$$\mathbf{x} = (S_I S_S S_{NO} S_{NH} S_{ND} S_{ALK} X_S X_{BH} X_{BA} X_P X_{ND}) \quad (32)$$

$$\mathbf{x}^{\text{in}} = (30 \ 40.23 \ 8.55 \ 19.07 \ 4.19 \ 5.5 \ 148.65 \ 2305.04 \ 126.85 \ 338.89 \ 8.67) \quad (33)$$

then, the 3 components ς_i of the reaction invariant vector ς are obtained from Eq. (11):

$$\begin{aligned} \varsigma_1 &= 2.79 \cdot (S_S + X_S) + (S_{NH} + S_{ND} + X_{ND}) \\ &\quad + 4.25 \cdot (X_{BH} + X_{BA}) + 20.04 \cdot X_P = 17677.73 \end{aligned} \quad (34)$$

$$\varsigma_2 = S_I = 30 \quad (35)$$

$$\varsigma_3 = 0.0714 \cdot (S_{NO} - S_{NH}) + S_{ALK} = 4.74 \quad (36)$$

As expected, it was found that S_I must necessarily be one of the algebraic variables of the reduced model. The remaining variables can be chosen arbitrarily; in this case, the variables S_{NH} and S_{ALK} are selected. Then, the model reduction implies replacing the original

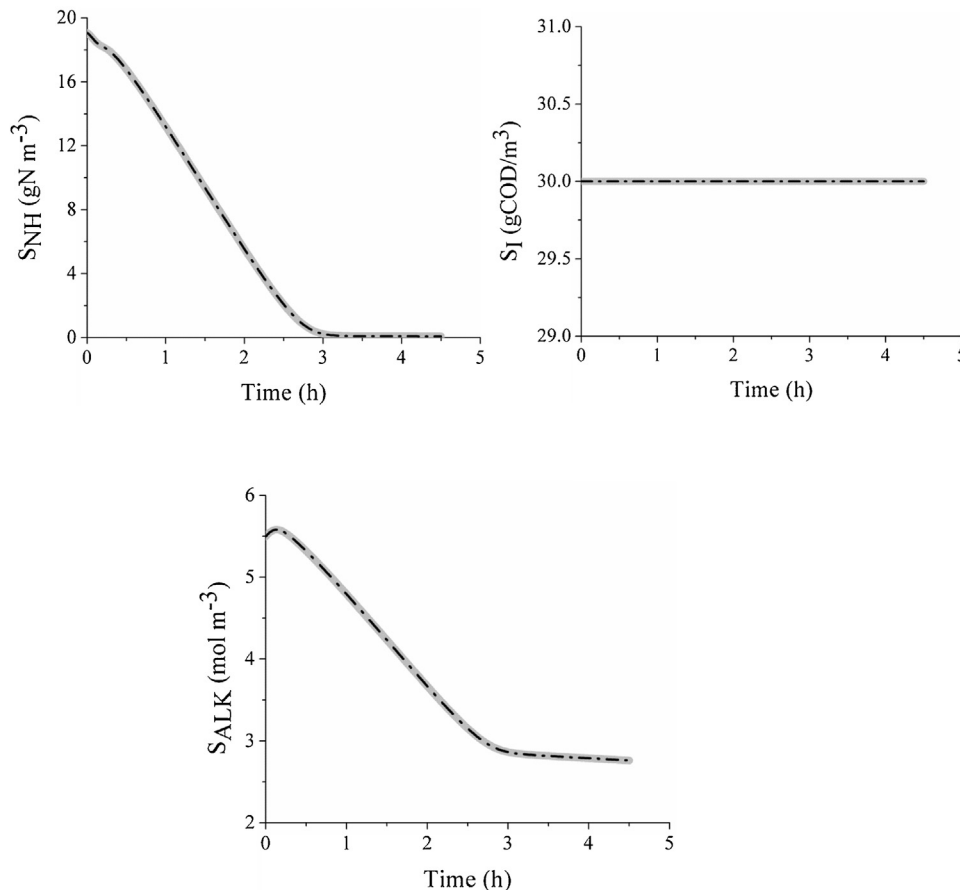


Fig. 2. Dynamics of the components S_{NH} , S_i , and S_{ALK} predicted by the original model (solid line) and the reduced model (dash-dotted line) for CS2.

nonlinear ODEs given by Eqs. (37)–(39):

$$\begin{aligned} \frac{dS_{NH}}{dt} = & (-i_{xb}) \cdot \mu_h \cdot \frac{S_S}{K_S + S_S} \cdot \frac{S_O}{K_{OH} + S_O} \cdot X_{BH} + \\ & (-i_{xb}) \cdot \mu_h \cdot \frac{S_S}{K_S + S_S} \cdot \frac{K_{OH}}{K_{OH} + S_O} \cdot \frac{S_{NO}}{K_{NO} + S_{NO}} \cdot \eta_g \cdot X_{BH} + \\ & \left(-i_{xb} - \frac{1}{y_A}\right) \cdot \mu_a \cdot \frac{S_{NH}}{K_{NH} + S_{NH}} \cdot \frac{S_O}{K_{OA} + S_O} \cdot X_{BA} + K_a \cdot S_{ND} \cdot X_{BH} \end{aligned} \quad (37)$$

$$\frac{dS_I}{dt} = 0 \quad (38)$$

$$\begin{aligned} \frac{dS_{ALK}}{dt} = & \left(\frac{-i_{xb}}{14}\right) \cdot \mu_h \cdot \frac{S_S}{K_S + S_S} \cdot \frac{S_O}{K_{OH} + S_O} \cdot X_{BH} + \\ & \left(\frac{1 - y_H}{14 \cdot 2.86 \cdot y_H} - \frac{i_{xb}}{14}\right) \cdot \mu_h \cdot \frac{S_S}{K_S + S_S} \cdot \frac{K_{OH}}{K_{OH} + S_O} \cdot \frac{S_{NO}}{K_{NO} + S_{NO}} \cdot \eta_g \cdot X_{BH} + \\ & \left(\frac{-i_{xb}}{14} - \frac{1}{y_A}\right) \cdot \mu_a \cdot \frac{S_{NH}}{K_{NH} + S_{NH}} \cdot \frac{S_O}{K_{OA} + S_O} \cdot X_{BA} + \frac{1}{14} \cdot K_a \cdot S_{ND} \cdot X_{BH} \end{aligned} \quad (39)$$

by the linear algebraic relationships given by Eqs. (40)–(42), respectively:

$$\begin{aligned} S_{NH} = & 17677.73 - 2.79 \cdot (S_S + X_S) - (X_{ND} + S_{ND}) \\ & - 4.25 \cdot (X_{BH} + X_{BA}) - 20.04 \cdot X_P \end{aligned} \quad (40)$$

$$S_I = 30 \quad (41)$$

$$S_{ALK} = 4.74 - 0.0714 \cdot (S_{NO} - S_{NH}) \quad (42)$$

The dynamics of components S_{NH} , S_I and S_{ALK} obtained by simulating the aerobic phase of a batch process with the original model and the resulting reduced model are compared in Fig. 2. The initial conditions ($t=0$) for the variables included into the reduction procedure (Eq. (32)) are given by Eq. (33) and for the variables that were not included are: $S_O^{in}=0 \text{ g O}_2 \text{ m}^{-3}$ and $X_I^{in}=980.32 \text{ g COD m}^{-3}$. A $k_L a$ value of 240 d^{-1} and the default ASM1 parameter values were used. It is observed that both models predict exactly the same dynamic behavior. As expected, both models predict the same dynamic behavior for the other components as well (not shown), since there the original ODEs are kept.

Although the reduction procedure was performed for a batch bioreactor with continuous aeration, the reduced model can simulate (exactly) the dynamic behavior of the original model for any aeration profile. Fig. 3 compares the simulation results for an intermittent aeration profile predicted by both models for a batch bioreactor.

4.3. Case study 3 (CS3): 5 reaction invariants

This case study deals with the largest possible reduction of the ASM1 model in batch reactors with the considered methodology, obtaining 5 reaction invariants; consequently, 5 states of the system can be represented by 5 linear algebraic relationships. For demonstration purposes, this reduction is applied to the anoxic phase of the reaction stage of a batch process; for instance, the

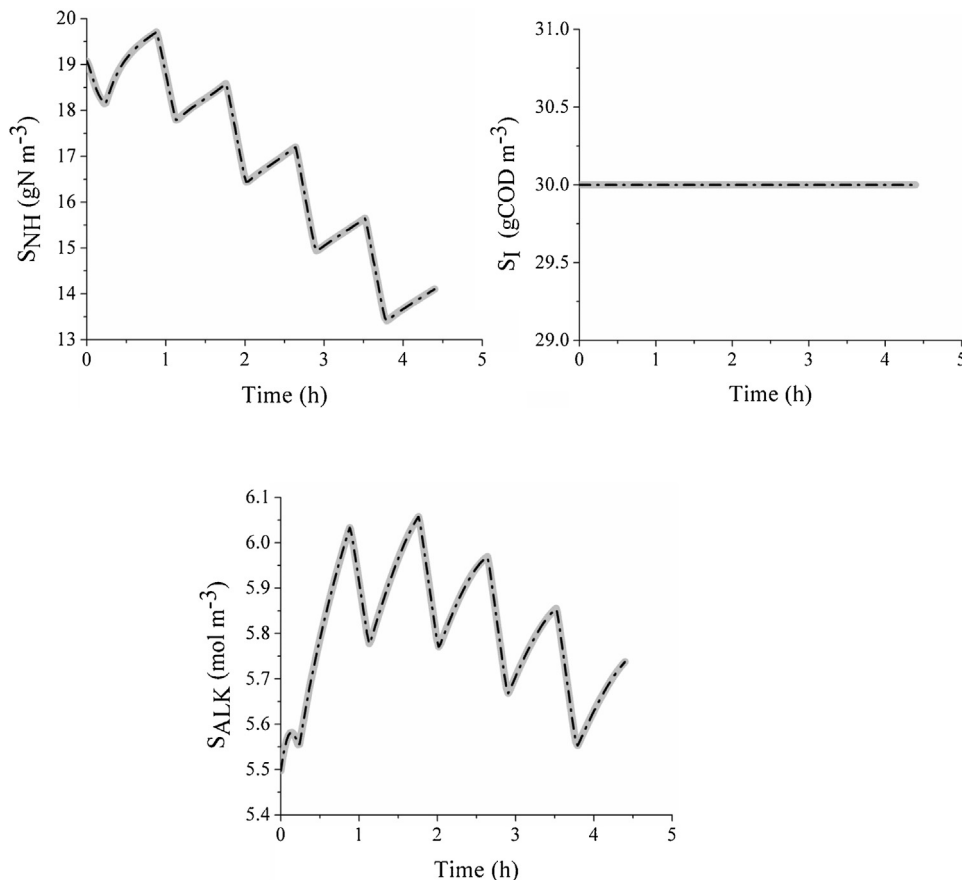


Fig. 3. Comparison of the dynamics of the components S_{NH} , S_I , and S_{ALK} predicted by the original model (solid line) and the reduced model (dash-dotted line) for an intermittent aeration profile.

anoxic phase of an activated sludge sequencing batch reactor (SBR) process (cyclic process of filling, reaction, settling, withdrawing and, eventually, idle) [37–42]. This is possible because the oxygen component S_O is incorporated into the reduction procedure without considering its liquid-gas transfer as no aeration is required in this treatment phase.

In this case, the system's stoichiometric coefficients matrix $\mathbf{C} \in R^{(13 \times 8)}$ is of rank 8, with 13 components and 8 reactions. The matrix \mathbf{A} to be found has the dimension $(13-8) \times 13$:

$$\mathbf{A} = \begin{pmatrix} a_{1,1} & \dots & a_{1,13} \\ \vdots & \ddots & \vdots \\ a_{5,1} & \dots & a_{5,13} \end{pmatrix} \quad (43)$$

The homogeneous linear system $\mathbf{A} \cdot \mathbf{C} = \mathbf{0}$ (Eq. (2)) consists of 40 equations and 65 unknowns; then, 25 free variables a_{ij} (set α) should be selected and assigned values h_{ij} , where h_{ij} either takes the value 0 or 1 (set β). The set α obtained by the G-J method and one of the sets β with five times the value "1" (the minimum number possible) generated by the *ad hoc* algorithm are:

$$\alpha = (a_{1,1}, a_{1,6}, a_{1,8}, a_{1,12}, a_{1,13}, a_{2,1}, a_{2,6}, a_{2,8}, a_{2,12}, a_{2,13}, a_{3,1}, a_{3,6}, a_{3,8}, a_{3,12}, a_{3,13}, a_{4,1}, a_{4,6}, a_{4,8}, a_{4,12}, a_{4,13}, a_{5,1}, a_{5,6}, a_{5,8}, a_{5,12}, a_{5,13})$$

$$\beta = (0100000100000011000000010)$$

Thus, the matrix \mathbf{Q} of dimension 65×65 (not shown) is obtained, whose last 25 rows correspond to the previous assignments; and the vector \mathbf{b} is obtained, which is formed by 40 null elements and the 25 elements of the set β : $\mathbf{b}^T = (\mathbf{0} \ \beta)$.

The vector \mathbf{w} and, consequently, the matrix \mathbf{A} of rank 5 to be found are obtained from Eqs. (8) and (9), respectively:

$$\mathbf{A} = \begin{pmatrix} 0 & 0 & 0.071 & -0.071 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0.51 & -1.73 & 1 & 1 & 0 & -0.6 & 0 & 0.51 & 0.55 & 0.55 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0.11 & 0.086 & 0 & 0 & 0 & 0.03 & 0 & 0.11 & 0.18 & 0.18 & 1 & 0 & 0 & 0 \end{pmatrix} \quad (44)$$

If the state vector \mathbf{x} and the initial condition vector \mathbf{x}^{in} are the following:

$$\mathbf{x} = (S_I S_S S_{NO} S_{NH} S_{ND} S_{ALK} S_O X_I X_S X_{BH} X_{BA} X_P X_{ND}) \quad (45)$$

$$\mathbf{x}^{\text{in}} = (30 \ 0.76 \ 25.23 \ 1.31 \ 0.64 \ 3.04 \ 3.82 \ 980.31 \ 38.46 \ 2375.87 \ 131.12 \ 345.17 \ 2.84) \quad (46)$$

then, the 5 components ζ_i of the reaction invariant vector ζ are obtained from Eq. (11):

$$\zeta_1 = 0.071 \cdot (S_{NO} - S_{NH}) + S_{ALK} = 4.74 \quad (47)$$

$$\zeta_2 = X_I = 980.32 \quad (48)$$

$$\zeta_3 = 0.51 \cdot (S_S + X_S) - 1.73 \cdot S_{NO} + S_{NH} + S_{ND} - 0.6 \cdot S_O + 0.55 \cdot (X_{BH} + X_{BA}) + X_{ND} = 1347.04 \quad (49)$$

$$\zeta_4 = S_I = 30 \quad (50)$$

$$\zeta_5 = 0.11 \cdot (S_S + X_S) + 0.086 \cdot S_{NO} + 0.03 \cdot S_O + 0.18 \cdot (X_{BH} + X_{BA}) + X_P = 814.93 \quad (51)$$

It is observed that S_I and X_I must necessarily be two of the algebraic variables of the reduced model. The remaining three variables are arbitrarily selected to be S_{ALK} , S_{ND} and S_{NO} in this case. Then, the model reduction implies replacing the original non-linear ODEs given by Eq. (52)–(56):

$$\begin{aligned} \frac{dS_{ALK}}{dt} &= \left(\frac{-i_{xb}}{14} \right) \cdot \mu_h \cdot \frac{S_S}{K_S + S_S} \cdot \frac{S_O}{K_{OH} + S_O} \cdot X_{BH} + \\ &\left(\frac{1 - y_H}{14 \cdot 2.86 \cdot y_H} - \frac{i_{xb}}{14} \right) \cdot \mu_h \cdot \frac{S_S}{K_S + S_S} \cdot \frac{K_{OH}}{K_{OH} + S_O} \cdot \frac{S_{NO}}{K_{NO} + S_{NO}} \cdot \eta_g \cdot X_{BH} + \\ &\left(\frac{i_{xb}}{14} - \frac{1}{y_A} \right) \cdot \mu_a \cdot \frac{S_{NH}}{K_{NH} + S_{NH}} \cdot \frac{S_O}{K_{OA} + S_O} \cdot X_{BA} + \frac{1}{14} \cdot K_a \cdot S_{ND} \cdot X_{BH} \end{aligned} \quad (52)$$

$$\frac{dX_I}{dt} = 0 \quad (53)$$

$$\begin{aligned} \frac{dS_{ND}}{dt} &= -(k_a \cdot S_{ND} \cdot X_{BH}) + \\ &K_H \cdot \frac{X_S / X_{BH}}{K_X + X_S / X_{BH}} \cdot \left(\frac{S_O}{K_{OH} + S_O} + \eta_h \cdot \frac{K_{OH}}{K_{OH} + S_O} \cdot \frac{S_{NO}}{K_{NO} + S_{NO}} \right) \cdot X_{BH} \cdot \left(\frac{X_{ND}}{X_S} \right) \end{aligned} \quad (54)$$

$$\frac{dS_I}{dt} = 0 \quad (55)$$

$$\begin{aligned} \frac{dS_{NO}}{dt} &= \left(\frac{1 - y_H}{2.86 \cdot y_H} \right) \cdot \mu_h \cdot \frac{S_S}{K_S + S_S} \cdot \frac{K_{OH}}{K_{OH} + S_O} \cdot \frac{S_{NO}}{K_{NO} + S_{NO}} \cdot \eta_g \cdot X_{BH} \\ &+ \left(\frac{1}{y_A} \right) \cdot \mu_a \cdot \frac{S_{NH}}{K_{NH} + S_{NH}} \cdot \frac{S_O}{K_{OA} + S_O} \cdot X_{BA} \end{aligned} \quad (56)$$

by the linear algebraic relationships given by Eqs. (57)–(61), respectively:

$$S_{ALK} = 4.74 - 0.071 \cdot (S_{NO} - S_{NH}) \quad (57)$$

$$X_I = 980.32 \quad (58)$$

$$S_{ND} = 1347.04 - 0.51 \cdot (S_S + X_S) + 1.73 \cdot S_{NO} - S_{NH} + 0.6 \cdot S_O - 0.55 \cdot (X_{BH} + X_{BA}) - X_{ND} \quad (59)$$

$$S_I = 30 \quad (60)$$

$$S_{NO} = 9475.93 - 1.28 \cdot (S_S + X_S) - 0.35 \cdot S_O - 2.09 \cdot (X_{BH} + X_{BA}) - 11.62 \cdot X_P \quad (61)$$

The dynamics of components S_{ALK} , X_I , S_{ND} , S_I and S_{NO} obtained by simulating the anoxic phase (i.e. a non-aerated process) of a bath reactor with the original model and the resulting reduced model are compared in Fig. 4. The initial conditions set for the variables included into the reduction procedure (Eq. (45)) are given by Eq. (46). A k_{La} value of 0 and the default ASM1 parameter values were used. It is again observed that both models predict exactly the same dynamic behavior. As expected, both models predict the same dynamic behavior for the other components as well (results not shown).

Then, in this case study, a reduced version of the ASM1 model consisting of 8 ODEs was obtained to describe the dynamic behavior of the anoxic phase of the reaction step of a batch process for C and N removal, rather than using the 13 ODEs of the original model.

5. Conclusions

The characteristics of the ASM1 model with respect to the number of reactions and components were appropriate to allow applying the methodology of model reduction based on reaction invariants.

The dynamic behaviors of the bioreactors simulated using the resulting reduced models were compared with respect to the “original” model for three case studies to obtain 1, 3 and 5 reaction invariants.

From a numerical point of view, this reduction may mean an improvement in the model initialization and/or solution for dynamic optimization since it allows replacing, for instance, the discretization of 5 highly *nonlinear differential* equations by 5 *linear*

algebraic equations in an equation-oriented algebraic modeling platform, such as GAMS.

From a conceptual point of view, a simpler model in terms of the number of linear constraints is at a first glance better or, at least, not worse for optimization purposes than a more complex (nonlinear) model since a lower number of bilinear terms (e.g.: $[S_s/(K_s + S_s)] \times [S_o/(K_{OH} + S_o)]$), and consequently, of non-convex constraints are present. It was shown that it is also possible to reduce the number of model parameters present in the resulting reduced model; however, all the stoichiometric coefficients of the original model must be known values when starting the reduction procedure. The reduction of the required computational time for simulating the three case studies was negligible i.e. the reduced model did not necessarily lead to faster simulation runs.

The model reduction methodology based on reaction invariants can be generally and straightforwardly applied to any closed biochemical or chemical reacting system (e.g. batch process) with the only condition that the number of components involved in the reaction mechanism is greater than the number of conversion processes. When such a reduction is possible, the reduced model

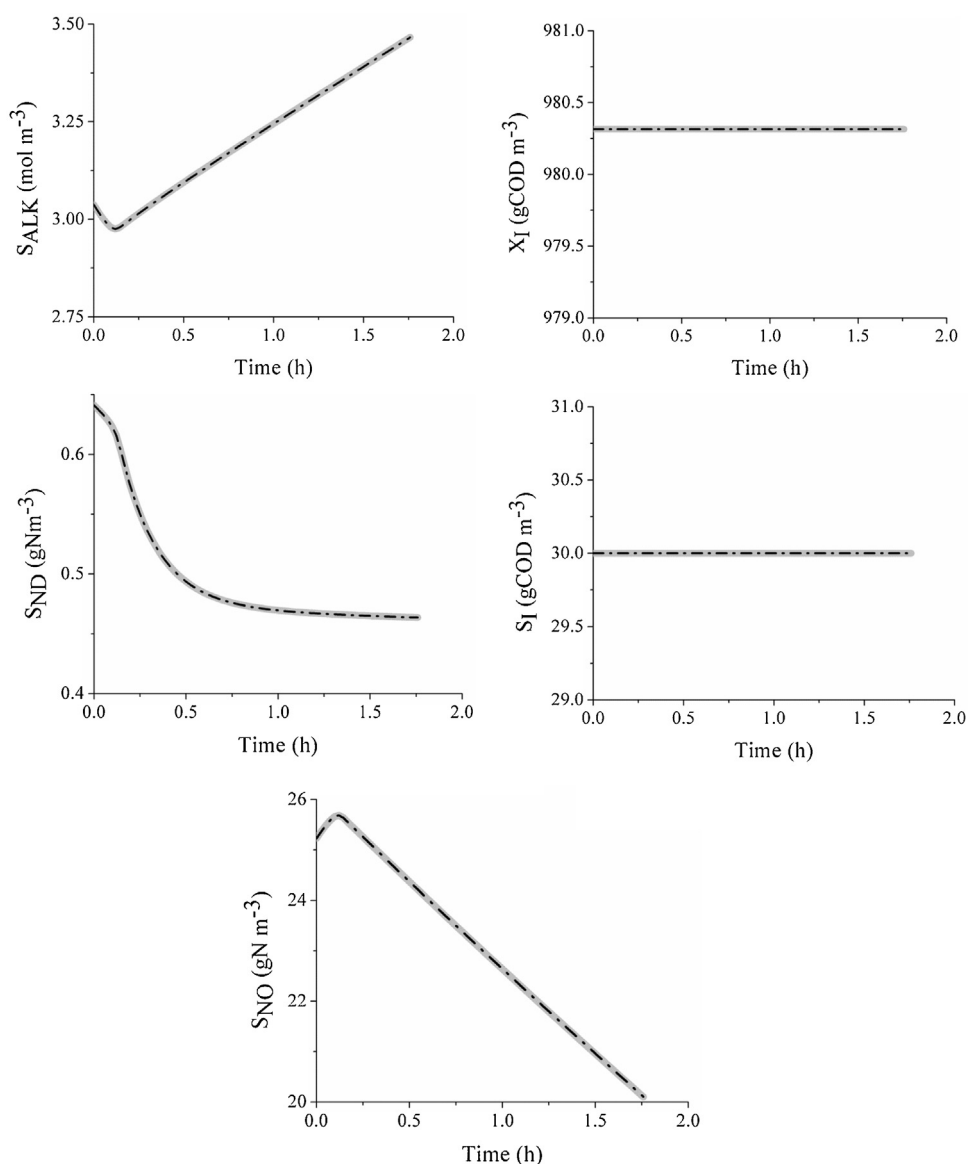


Fig. 4. Dynamics of the components S_{ALK} , X_i , S_{ND} , S_i , and S_{NO} predicted by the original model (solid line) and the reduced model (dash-dotted line) for CS3.

predicts the exact dynamics of the original model. In other words, the same dynamic trajectory as predicted by the original model is obtained as a result of (linear) mathematical transformations, and not just an approximate trajectory as a result of simplifying the assumptions of the original model, which is the case for many other reduced models obtained using other techniques.

The reaction invariants are also used in the invariant manifold approach for reduction of dynamic models that describe continuous flow reactors. This issue will be addressed in a further paper considering a continuous-flow activated sludge bioreactor described by the ASM1 model. Methodologically, this paper forms a first part of that work.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jece.2016.07.007>.

References

- [1] M. Henze, C.P.L. Grady Jr., W. Gujer, G.V.R. Marais, T. Matsuo, A general model for single-sludge wastewater treatment systems, *Water Res.* 21 (1987) 505–515, doi:[http://dx.doi.org/10.1016/0043-1354\(87\)90058-3](http://dx.doi.org/10.1016/0043-1354(87)90058-3).
- [2] W. Gujer, M. Henze, T. Mino, T. Matsuo, M.C. Wentzel, G. v. R. Marais, The activated sludge model No. 2: biological phosphorus removal, *Water Sci. Technol.* 31 (1995) 1–11, doi:[http://dx.doi.org/10.1016/0273-1223\(95\)00175-M](http://dx.doi.org/10.1016/0273-1223(95)00175-M).
- [3] M. Henze, W. Gujer, T. Mino, T. Matsuo, M.C. Wentzel, G. v. R. Marais, M.C.M. Van Loosdrecht, Activated sludge model No.2D, ASM2D, *Water Sci. Technol.* 39 (1999) 165–182, doi:[http://dx.doi.org/10.1016/S0273-1223\(98\)00829-4](http://dx.doi.org/10.1016/S0273-1223(98)00829-4).
- [4] W. Gujer, M. Henze, T. Mino, M. van Loosdrecht, Activated sludge model No. 3, *Water Sci. Technol.* 39 (1999) 183–193, doi:[http://dx.doi.org/10.1016/S0273-1223\(98\)00785-9](http://dx.doi.org/10.1016/S0273-1223(98)00785-9).
- [5] O. Glenn, *A Treatise on the Theory of Invariants*, The Athenaeum Press, Ginn and Company, Boston, USA, 1915. <https://ia601406.us.archive.org/3/items/atreatiseontheo00glengoog/atreatiseontheo00glengoog.pdf>.
- [6] O. Glenn, *A Treatise on the Theory of Invariants*, Forgotten Books, Boston, USA, 2012.
- [7] O.A. Asbjørnsen, M. Field, Response modes of continuous stirred tank reactors, *Chem. Eng. Sci.* 25 (1970) 1627–1636, doi:[http://dx.doi.org/10.1016/0009-2509\(70\)80054-9](http://dx.doi.org/10.1016/0009-2509(70)80054-9).
- [8] O.A. Asbjørnsen, Reaction invariants in the control of continuous chemical reactors, *Chem. Eng. Sci.* 27 (1972) 709–717, doi:[http://dx.doi.org/10.1016/0009-2509\(72\)85007-3](http://dx.doi.org/10.1016/0009-2509(72)85007-3).
- [9] M. Fjeld, O.A. Asbjørnsen, K.J. Åström, Reaction invariants and their importance in the analysis of eigenvectors, state observability and controllability of the continuous stirred tank reactor, *Chem. Eng. Sci.* 29 (1974) 1917–1926, doi:[http://dx.doi.org/10.1016/0009-2509\(74\)85009-8](http://dx.doi.org/10.1016/0009-2509(74)85009-8).
- [10] B. Srinivasan, M. Amrhein, D. Bonvin, Reaction and flow variants/invariants in chemical reaction systems with inlet and outlet streams, *AIChE J.* 44 (1998) 1858–1867, doi:<http://dx.doi.org/10.1002/aic.690440815>.
- [11] S.B. Gadewar, M.F. Doherty, M.F. Malone, Reaction invariants and mole balances for plant complexes, *Ind. Eng. Chem. Res.* 41 (2002) 3771–3783.
- [12] K.V. Waller, P.M. Makila, Chemical reaction invariants and variants and their use in reactor modeling, simulation, and control, *Ind. Eng. Chem. Process Des. Dev.* 20 (1981) 1–11, doi:<http://dx.doi.org/10.1021/i200012a001>.
- [13] D. Barbosa, M.F. Doherty, New set of composition variables for the representation of reactive-phase diagrams, *Proc. R. Soc. Lond. Ser. Math. Phys. Sci.* 413 (1987) 459–464.
- [14] D. Barbosa, M.F. Doherty, Design and minimum-reflux calculations for single-feed multicomponent reactive distillation columns, *Chem. Eng. Sci.* 43 (1988) 1523–1537, doi:[http://dx.doi.org/10.1016/0009-2509\(88\)85144-3](http://dx.doi.org/10.1016/0009-2509(88)85144-3).
- [15] S. Ung, M.F. Doherty, Calculation of residue curve maps for mixtures with multiple equilibrium chemical reactions, *Ind. Eng. Chem. Res.* 34 (1995) 3195–3202.
- [16] S. Ung, M.F. Doherty, Synthesis of reactive distillation systems with multiple equilibrium chemical reactions, *Ind. Eng. Chem. Res.* 34 (1995) 2555–2565.
- [17] S. Ung, M.F. Doherty, Vapor-liquid phase equilibrium in systems with multiple chemical reactions, *Chem. Eng. Sci.* 50 (1995) 23–48, doi:[http://dx.doi.org/10.1016/0009-2509\(94\)00180-Y](http://dx.doi.org/10.1016/0009-2509(94)00180-Y).
- [18] S.B. Gadewar, M.F. Doherty, M.F. Malone, A systematic method for reaction invariants and mole balances for complex chemistries, *Comput. Chem. Eng.* 25 (2001) 1199–1217, doi:[http://dx.doi.org/10.1016/S0098-1354\(01\)00695-0](http://dx.doi.org/10.1016/S0098-1354(01)00695-0).
- [19] S. Grüner, M. Mangold, A. Kienle, Dynamics of reaction separation processes in the limit of chemical equilibrium, *AIChE J.* 52 (2006) 1010–1026, doi:<http://dx.doi.org/10.1002/aic.10686>.
- [20] T.D. Vu, A. Seidel-Morgenstern, S. Grüner, A. Kienle, Analysis of ester hydrolysis reactions in a chromatographic reactor using equilibrium theory and a rate model, *Ind. Eng. Chem. Res.* 44 (2005) 9565–9574, doi:<http://dx.doi.org/10.1021/ie050256j>.
- [21] Y.-S. Huang, K. Sundmacher, Z. Qi, E.-U. Schlünder, Residue curve maps of reactive membrane separation, *Chem. Eng. Sci.* 59 (2004) 2863–2879, doi:<http://dx.doi.org/10.1016/j.ces.2004.04.018>.
- [22] D. Flockerzi, A. Bohmann, A. Kienle, On the existence and computation of reaction invariants, *Chem. Eng. Sci.* 62 (2007) 4811–4816, doi:<http://dx.doi.org/10.1016/j.ces.2007.05.003>.
- [23] M. Aggarwal, S. Balaji, B.E. Ydstie, Invariant based modeling and control of multi-phase reactor systems, *J. Process Control.* 21 (2011) 1390–1406, doi:<http://dx.doi.org/10.1016/j.jprocont.2011.07.008>.
- [24] S. Srinivasan, J. Billeter, D. Bonvin, Variant and invariant states for reaction systems, *IFAC Proc.* 46 (2013) 102–107, doi:<http://dx.doi.org/10.3182/20130714-3-FR-4040.00020>.
- [25] D. Rodríguez, S. Srinivasan, J. Billeter, D. Bonvin, Variant and invariant states for chemical reaction systems, *Comput. Chem. Eng.* 73 (2015) 23–33, doi:<http://dx.doi.org/10.1016/j.compchemeng.2014.10.009>.
- [26] K. Stamatelatos, L. Syrou, C. Kravaris, G. Lyberatos, An invariant manifold approach for CSTR model reduction in the presence of multi-step biochemical reaction schemes. Application to anaerobic digestion, *Chem. Eng. J.* 150 (2009) 462–475, doi:<http://dx.doi.org/10.1016/j.cej.2009.01.033>.
- [27] M.N. Cruz Bournazou, H. Arellano-García, G. Wozny, G. Lyberatos, C. Kravaris, ASM3 extended for two-step nitrification-denitrification: a model reduction for sequencing batch reactors, *J. Chem. Technol. Biotechnol.* 87 (2012) 887–896, doi:<http://dx.doi.org/10.1002/jctb.3694>.
- [28] B. Ráduly, K.V. Gernaey, A.G. Capodaglio, P.S. Mikkelsen, M. Henze, Artificial neural networks for rapid WWTP performance evaluation: methodology and case study, *Environ. Model. Softw.* 22 (2007) 1208–1216, doi:<http://dx.doi.org/10.1016/j.envsoft.2006.07.003>.
- [29] M. Amrhein, Reaction and flow variants/invariants for the analysis of chemical reaction data, PhD Thesis, École Polytechnique Fédérale de Lausanne, 1998.
- [30] G. Sin, P. Ödman, N. Petersen, A.E. Lantz, K.V. Gernaey, Matrix notation for efficient development of first-principles models within PAT applications: integrated modeling of antibiotic production with *Streptomyces coelicolor*, *Biotechnol. Bioeng.* 101 (2008) 153–171, doi:<http://dx.doi.org/10.1002/bit.21869>.
- [31] W. Henze, T. Gujer, M.C.M. Mino, Activated Sludge Models ASM1, ASM2, ASM2d and ASM3, IWA Publishing, London, England, 2000.
- [32] H.J. Noorman, J.J. Heijnen, C.K.A.M. Luyben, Linear relations in microbial reaction systems: a general overview of their origin, form, and use, *Biotechnol. Bioeng.* 38 (1991) 603–618.
- [33] W. Gujer, T.A. Larsen, The implementation of biokinetics and conservation principles in ASIM, *Water Sci. Technol.* 31 (1995) 257–266, doi:[http://dx.doi.org/10.1016/0273-1223\(95\)00198-V](http://dx.doi.org/10.1016/0273-1223(95)00198-V).
- [34] P. Barton, C. Pantelides, gPROMS – a combined discrete/continuous modelling environment for chemical processing systems, *Simul. Ser.* 25 (1993) 25–34.
- [35] Process Systems Enterprise Ltd, gPROMS Introductory User Guide, Release 2.3.1, Process Systems Enterprise Limited, London, UK, 2004.
- [36] Process Systems Enterprise Ltd, gPROMS Advanced User Guide, Release 2.3, Process Systems Enterprise Limited, London, UK, 2004.
- [37] M. Mauricio-Iglesias, A.K. Vangsgaard, K.V. Gernaey, B.F. Smets, G. Sin, A novel control strategy for single-stage autotrophic nitrogen removal in SBR, *Chem. Eng. J.* 260 (2015) 64–73, doi:<http://dx.doi.org/10.1016/j.cej.2014.08.069>.
- [38] Y.-H. Kim, C. Yoo, I.-B. Lee, Optimization of biological nutrient removal in a SBR using simulation-based iterative dynamic programming, *Chem. Eng. J.* 139 (2008) 11–19, doi:<http://dx.doi.org/10.1016/j.cej.2007.07.070>.
- [39] N. Artan, D. Orhon, Mechanism and Design of Sequencing Batch Reactors for Nutrient Removal, IWA Publishing, 2005.
- [40] D.S. Lee, G. Sin, G. Insel, I. Nopens, P.A. Vanrolleghem, Model-based optimization of a sequencing batch reactor for advanced biological wastewater treatment, in: I-SN, J.M.P. Hyun-Ku Rhee (Eds.), *Stud. Surf. Sci. Catal., Elsevier*, 2016, pp. 165–168. (accessed 05.11.14) <http://www.sciencedirect.com/science/article/pii/S0167299106815594>.
- [41] S. Mace, J. Mata-Alvarez, Utilization of SBR technology for wastewater treatment: an overview, *Ind. Eng. Chem. Res.* 41 (2002) 5539–5553.
- [42] R.L. Irvine, J. Ketchum, Sequencing batch reactors for biological wastewater treatment, *Crit. Rev. Environ. Control.* 18 (1988) 255–294.