

Modeling of partial nitrification and denitrification in an SBR for leachate treatment without carbon addition

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Abstract A process of partial nitrification and denitrification in a sequencing batch reactor (SBR) treating leachate was simulated by applying a modified version of activated sludge model no. 3 (ASM3), named ASM3_2step. This model modifies the ASM3 model by separating nitrification and denitrification into two steps with nitrite as an intermediate substrate. Three periods, including long term period, steady state and cycle evolution, were used for calibration. Three main processes were observed, including biomass production, nitrification (focusing on nitrite accumulation) and denitrification. The kinetic and stoichiometric parameters (μ_{A_NH} , Y_{A_NH} , $Y_{A_NO_2}$, $Y_{H_O_2}$, b_A , K_{A_NH}), were determined from biokinetic and respirometry tests. Some of the default values of kinetic and stoichiometric parameters available in the ASM3 model and in the literature were kept constant, while some others were adjusted step by step until observed state variables fit with experimental data. The maximum specific growth rate of nitrite oxidizing bacteria (0.108 day^{-1}) (simulated by the model) and that of ammonium oxidizing bacteria (0.61 day^{-1}) (from biokinetic tests) are the parameters which have the highest influence on the nitrite accumulation, even more than oxygen supply intensity or K_{La} value. Other important parameters were K_{AO_NH} and $K_{AO_NO_2}$, calibrated at the values of 1.37 and $1.59 \text{ mg O}_2/\text{L}$,

respectively. The modified model and values of the kinetic and stoichiometric parameters obtained from the modeling process will be used for optimization of the partial nitrification in the next study.

Keywords Modeling · Nitrite accumulation · Leachate · SBR

List of symbols

Model parameters

k_h	Hydrolysis rate constant [g COD/(g COD day)]
$b_{A_O_2}$	Aerobic endogenous respiration rate of X_A (1/day)
F_{BOD_COD}	Conversion factor BOD/COD (g COD/g COD)
f_{S_I}	Production of S_I in hydrolysis
f_{X_I}	Production of X_I in aerobic endogenous respiration
i_{N_BM}	N content of biomass X_H , X_A (g N/g COD)
$i_{N_S_I}$	N content of S_I (g N/g COD)
$i_{N_S_S}$	N content of S_S (g N/g COD)
$i_{N_X_I}$	N content of X_I (g N/g COD)
$i_{N_X_S}$	N content of X_S (g N/g COD)
i_{TS_BM}	TSS to COD ratio for biomass X_H , X_A
$i_{TS_S_{TO}}$	TSS to COD ratio for $X_{S_{TO}}$ based on PHB
$i_{TS_X_I}$	TSS to COD ratio for X_I
$i_{TS_X_S}$	TSS to COD ratio for X_S
K_{A_NH}	Ammonium substrate concentration for X_{A_NH} (g NH_3 N/m ³)
$K_{A_NO_2}$	Ammonium substrate concentration for $X_{A_NO_2}$ (g NH_3 N/m ³)
$K_{A_O_NH}$	Oxygen saturation for X_{A_NH} (g O_2 /m ³)
$K_{A_O_NO_2}$	Oxygen saturation for $X_{A_NO_2}$ (g O_2 /m ³)

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K_{HCO}	Bicarbonate saturation constant of X_{H} (g COD/m ³)
K_{NH}	Ammonium saturation as nutrient (g NH ₃ N/m ³)
K_{NO}	Saturation constant for S_{NO} (g NO ₃ N/m ³)
K_{O}	Saturation constant for S_{O} (g O ₂ /m ³)
K_{S}	Saturation constant for substrate S_{S} (g COD/m ³)
K_{STO}	Storage rate constant (1/day)
K_{STO}	Saturation constant for X_{STO} (g COD/m ³)
$\mu_{\text{A_NH}}$	Autotrophic max. growth rate of $X_{\text{A_NH}}$ (1/day)
$\mu_{\text{A_NO}_2}$	Autotrophic max. growth rate of $X_{\text{A_NO}_2}$ (1/day)
$\mu_{\text{H_NO}_2}$	Heterotrophic max. growth rate of $X_{\text{H_NO}_2}$ (1/day)
$\mu_{\text{H_NO}_3}$	Heterotrophic max. growth rate of $X_{\text{H_NO}_3}$ (1/day)
n_{NO}	Anoxic reduction factor
$S_{\text{O_Sat}}$	Oxygen saturation concentration (g/m ³)
$Y_{\text{A_NH}}$	Yield of $X_{\text{A_NH}}$ per NO ₃ -N (g COD/g N)
$Y_{\text{A_NO}_2}$	Yield of $X_{\text{A_NO}_2}$ per NO ₃ -N (g COD/g N)
$Y_{\text{H_NO}}$	Anoxic yield of heterotrophic biomass per X_{STO} (g COD/g COD)
$Y_{\text{H_NO}_2}$	Anoxic yield of $X_{\text{H_NO}_2}$ per X_{STO} (g COD/g COD)
$Y_{\text{H_NO}_3}$	Anoxic yield of $X_{\text{H_NO}_3}$ per X_{STO} (g COD/g COD)
$Y_{\text{H_O}_2}$	Aerobic yield of heterotrophic biomass per X_{STO} (g COD/g COD)
$Y_{\text{STO_NO}}$	Anoxic yield of stored product per S_{S} (g COD/g COD)
$Y_{\text{STO_O}_2}$	Aerobic yield of stored product per S_{S} (g COD/g COD)
K_{la}	Oxygen transfer coefficient (1/day)

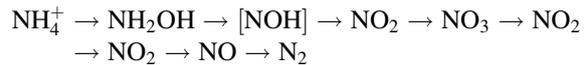
Model variables

S_{S}	Readily biodegradable organic (mg COD/L)
X_{S}	Slowly biodegradable organic (mg COD/L)
S_{I}	Inert soluble organic (mg COD/L)
X_{I}	Inert insoluble organic (mg COD/L)
S_{NH_4}	Ammonium (mg N/L)
S_{NO_2}	Nitrite (mg N/L)
S_{NO_3}	Nitrate (mg N/L)
S_{N_2}	Nitrogen gas (mg N/L)
$X_{\text{A_NH}}$	Ammonium oxidizing bacteria (mg COD/L)
$X_{\text{A_NO}_2}$	Nitrite oxidizing bacteria (mg COD/L)
$X_{\text{H_NO}_2}$	Nitrite denitrifying bacteria (mg COD/L)
$X_{\text{H_NO}_3}$	Nitrate denitrifying bacteria (mg COD/L)
X_{STO}	Cell internal storage product of heterotrophic organisms (mg COD/L)
X_{TSS}	Total suspended solid (mg SS/L)

Introduction

Leachate treatment is an important issue in many countries including Vietnam, where numerous landfill sites are located. Due to the high pluviometry, a large amount of leachates are produced every day with high concentrations of polluted substrates, especially nitrogen in the form of ammonium [27]. Conventional biological treatment for ammonium removal has high operation costs, due especially to the amount of oxygen required for nitrification and the amount of carbon needed for denitrification.

The possible metabolic pathways for conventional nitrification and denitrification are [17]:



The complete nitrification reaction consumes a large amount of oxygen, requiring 4.57 g oxygen for each gram of NH₄⁺-N oxidized. During denitrification, the requirement of organic carbon is significant. This can be expensive if the C/N ratio of wastewater is low, since a large amount of external carbon, such as methanol, is then required [21, 23, 26].

Partial nitrification is the oxidation of ammonium to nitrite, but not to nitrate [26]. Because nitrite is an intermediary compound in both steps, nitrification up to nitrite can be followed by nitrite denitrification [8].

The process is cost-effective since it needs less aeration (for nitrification) and less external carbon, such as methanol, as an electron donor source (for denitrification) in the case of a low C/N ratio [19, 26].

A number of studies on the partial nitrification process have shown similar benefits: a 20–30% savings in oxygen consumption and a 40% reduction in the organic carbon requirement [8, 19, 20, 21, 23]. In addition, this process could save 30–40% of reactor volume [24]. It also has been noticed that the denitrification of nitrite is 1.5–2 times faster than when carried out starting from nitrate [1].

The IWA (previously IAWQ) task group on mathematical modeling of activated sludge processes has proposed the activated sludge models (ASMs) to simulate the processes involved in biological carbon, nitrogen and phosphorus removal in municipal wastewater treatment plants, beginning with ASM1 in 1987 [14] as the first product. This model has been very successful in describing the behavior of activated sludge processes for nitrogen and organic matter removal. The revised version, activated sludge model no. 3 (ASM3), has been recently completed [13] for biological N removal. ASM3 has basically the same goals as ASM1 but it corrects some defects of ASM1 by including other processes related to the storage of organic substrates in heterotrophic organisms, assuming that the readily biodegradable substrate (S_{S}) is first taken up

and stored into an internal cell polymer component (X_{STO}) which is then used for growth. In addition, the lysis (decay) process is modified to be an endogenous respiration process.

A sequencing batch reactor (SBR) is a fill-and-draw type reactor system involving a single complete mix reactor in which all steps of the activated-sludge process occur [9, 22]. During SBR operation the processes are carried out sequentially in the same tank [22]. Therefore, the distribution of substrate concentration along the length (space) of a conventional activated plant varies with time. Several studies done in SBRs with partial nitrification [3, 7, 11, 12] have showed good applications of this technique.

This study has the following objectives:

Modification of the original ASM3 model to the ASM3_2step model, in which nitrification and denitrification are separated into two steps, with nitrite as an intermediate substrate;

Modelling of partial nitrification and denitrification (in case of no carbon addition) in an SBR bench—scale to obtain real values of some kinetic and stoichiometric parameters of the nitrification; these will be used to optimize the partial nitrification process in a future study.

Materials and methods

Materials

SBR bench-scale

The bench-scale pilot is described in more detail in a previous paper [18]. The SBR bench-scale is a set of experimental equipment including the following components: Buffer tank, collection tank, SBR tank, electronic controlling box, pump and pipes, mixer, and online measurement devices (DO, pH, ORP, DO controller device to maintain a stable DO concentration during nitrification process).

A complete working cycle (12 h) of the SBR includes 5 phases: filling (5 min), reaction (aeration + mixing) (355 + 120 min), settling (170 min), wasting (with sludge wasting) (5 min) and idle (65 min) (Fig. 1). During the calibration and validation period, working volumes were 7 and 6 L, corresponding to a hydraulic residence time (HRT) of 0.7 and 0.75 days, respectively; solid retention time (SRT) was kept around 46 days.

Leachate and sludge

Leachate used for this study was collected at the collection ponds in the Nam Son landfill site, Hanoi, once for calibration and another time for validation. Characteristics of leachates used for the calibration and validation periods are presented in Table 1 [27].

Activated sludge

Sludge was collected at Domestic WWTP Kim Lien—Truc Bach, Hanoi, Vietnam. This sludge was continuously aerated and fed with leachate, NH_4Cl and alkalinity $NaHCO_3$. During 2 months, it has shown good ammonium removal activity (nitrification rate was about $400\text{ mg } NH_4^+/\text{day}$).

WEST program

WEST (World Wide Engine for Simulation, Training and Automation) (HEMMIS.COM, http://www.hemmis.com/products/west/default_west.htm) is a general modelling and simulation environment that can be used together with a dedicated model. In the field of wastewater treatment, it can be used with a specific model base. The software is composed of three main elements: the model base, the configuration builder and the experimentation environment. The model base used in this study is specific for biological wastewater treatment, especially in 2 steps—nitrification and denitrification. This software also includes modules such as parameter estimation and sensitivity analysis that facilitate model development.

Fig. 1 Working processes in SBR

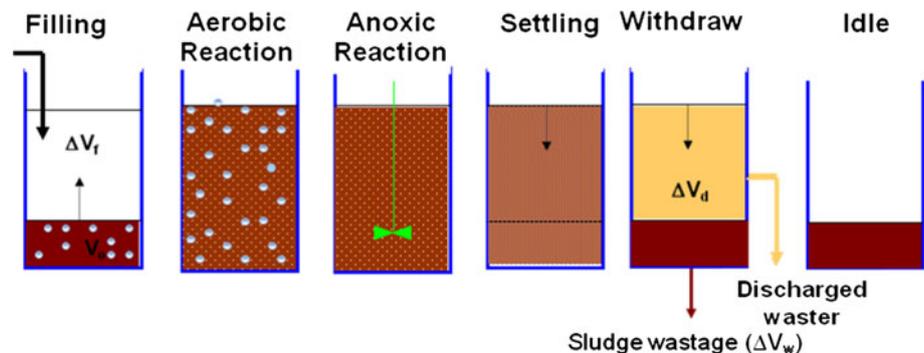


Table 1 Characteristics of the studied leachates

Parameters	Unit	Calibration	Validation
NH ₄ ⁺	mg N/L	335	546
NO ₂ ⁻	mg N/L	0.203	0.475
NO ₃ ⁻	mg N/L	0.4	0.3
TKN	mg N/L	346	561
COD	mg O ₂ /L	350	601
BOD _{5,27}	mg O ₂ /L	55	90
Alkalinity	mg CaCO ₃ /L	2370	4520
T-P	mg P/L	5.51	9.083
pH	–	8.44	8.56
Cl ⁻	mg/L	602	1225
SO ₄ ²⁻	mg/L	25	42

Methods

Determination of the hydrodynamic and biological processes of SBR

1. Measurement of gas–liquid mass transfer coefficients K_{La} in the media with and without biomass according to the American Society of Civil Engineering [6] procedure.
2. Determination of the mixing time by recording the time needed for the system to reach 95% of final conductivity after a pulse salt (tracer) addition.
3. Determination of sludge volume index (SVI) and settling velocity of the sludge [5].
4. Determination of sludge concentration [5] and nitrifying bacteria composition (critical dilution and cultivation in an MPA environment).
5. Determination of some kinetic parameters of biomass [22].

Mathematical model

The mathematical model of the process for the whole study is described by a modified *ASM3 Model-Peterson Matrix* [16] named *ASM3_2step*. In this model, the nitrification and denitrification processes were separated into two steps, in which nitrite is the intermediate product/substrate.

Application of calibration protocols

A protocol for calibration of the partial nitrification and denitrification process was applied in this study. This protocol was established from the combination of two protocols from two sources: BIOMATH (Department of Applied Mathematics, Biometrics and Process Control, Ghent University, Belgium) and STOWA (The Dutch Foundation of Applied Water Resource, The Netherlands).

Experimental approach

All off-line measurements followed Standard Methods for the Examination of Water and Wastewater [4, 5] (see also Table 1). The probes used are described in Hoang et al. [18].

Calibration of partial nitrification and denitrification process

Model definition

Mass transfer

The oxygen transfer coefficient (K_{La}) tests performed directly in the SBR during the filling aerated phase provided a filling K_{La} value of 27.5 and 28.48 h⁻¹ for the model in the calibration (working volume is 7 L) and validation (working volume is 6 L) periods.

Settler

As the sludge had been used for some previous experiments, the SVI at the beginning of calibration period was already good (99.8 mL g⁻¹). The sedimentation phase in the SBR was oversized, providing enough time for the sludge to settle before drawing. There was no change in ammonium concentration during the settling period. Hence, the reaction could be negligible for calibration of the nitrification process.

Kinetic, stoichiometric parameters and processes in ASM3_2step

The *ASM3_2step* model differs from the original model in that nitrification and denitrification are separated into two steps, with nitrite as an intermediate substrate. For example, from the nitrification process in *ASM3*, we have two correlative processes in *ASM3_2step*: aerobic growth of X_{A_NH} and aerobic growth of $X_{A_NO_2}$. From that, we have to separate *ASM3* parameters and variables to those related to *ASM3_2step*, which are highlighted in green rectangles. In the *ASM3_2step* model, there are 20 processes including 45 kinetic and stoichiometric parameters, 17 state variables. The main processes that are calibrated are given in Table 2.

Aeration and anoxic respiration processes of nitrifying and denitrifying bacteria, and anoxic respiration of nitrifying bacteria are not presented. Kinetic, stoichiometric parameters and variables (denitrifying bacteria) of the denitrification process are separated into two steps for nitrite and nitrate, but they are set up at the same values corresponding to each step.

Table 2 Main processes in the ASM3-2step

Processes	Process rate
1 Aeration storage of COD	$k_{STO} \times \frac{S_O}{K_O + S_O} \times \frac{S_S}{K_S + S_S} \times (X_{HNO_2} + X_{HNO_3})$
2 Anoxic storage of COD	$k_{STO} \times n_{NO} \times \frac{K_O}{K_O + S_O} \times \frac{S_{NO_2} + S_{NO_3}}{K_{NO} + S_{NO_2} + S_{NO_3}} \times \frac{S_S}{K_S + S_S} \times (X_{HNO_2} + X_{HNO_3})$
3 Aeration	$Kla_{Actuel} \times (S_{O_Sat} - S_O)$
4 Aeration growth of X_{A_NH}	$\mu_{A_NH} \times \frac{S_O}{K_{AO_NH} + S_O} \times \frac{S_{NH}}{K_{A_NH} + S_{NH}} \times \frac{S_{ALK}}{K_{A_HO} + S_{ALK}} \times X_{A_NH}$
5 Aeration growth of $X_{A_NO_2}$	$\mu_{A_NO_2} \times \frac{S_O}{K_{AO_NO_2} + S_O} \times \frac{S_{NO_2}}{K_{A_NO_2} + S_{NO_2}} \times \frac{S_{ALK}}{K_{A_OH} + S_{ALK}} \times X_{A_NO_2}$
6 Aeration growth of $X_{H_NO_2}$	$\mu_{H_NO_2} \times \frac{S_O}{K_O + S_O} \times \frac{S_{NH}}{K_{NH} + S_{NH}} \times \frac{S_{ALK}}{K_{HO} + S_{ALK}} \times \frac{X_{STO} / X_{H_NO_2}}{K_{STO} + X_{STO} / X_{HNO_2}} \times X_{H_NO_2}$
7 Aeration growth of $X_{H_NO_3}$	$\mu_{H_NO_3} \times \frac{S_O}{K_O + S_O} \times \frac{S_{NH}}{K_{NH} + S_{NH}} \times \frac{S_{ALK}}{K_{HO} + S_{ALK}} \times \frac{X_{STO} / X_{H_NO_3}}{K_{STO} + X_{STO} / X_{HNO_3}} \times X_{H_NO_3}$
8 Anoxic growth of $X_{H_NO_2}$	$\mu_{H_NO_2} \times n_{NO} \times \frac{K_O}{K_O + S_O} \times \frac{S_{NO_2}}{K_{NO} + S_{NO_2}} \times \frac{S_{NH}}{K_{NH} + S_{NH}} \times \frac{S_{ALK}}{K_{HO} + S_{ALK}} \times \frac{X_{STO} / X_{H_NO_2}}{K_{STO} + X_{STO} / X_{H_NO_2}} \times X_{H_NO_2}$
9 Anoxic growth of $X_{H_NO_3}$	$\mu_{H_NO_3} \times n_{NO} \times \frac{K_O}{K_O + S_O} \times \frac{S_{NO_3}}{K_{NO} + S_{NO_3}} \times \frac{S_{NH}}{K_{NH} + S_{NH}} \times \frac{S_{ALK}}{K_{HO} + S_{ALK}} \times \frac{X_{STO} / X_{H_NO_3}}{K_{STO} + X_{STO} / X_{H_NO_3}} \times X_{H_NO_3}$

Table 3 Kinetic and stoichiometric parameters at 20.2 and 25.98°C

	Unit	Calibration (at 20.2°C)			Validation (at 25.98°C)		
		X_{A_NH}	$X_{A_NO_2}$	Overall	X_{A_NH}	$X_{A_NO_2}$	Overall
K_{NH}	mg N/L	1.32	–	1.35	1.32	–	1.35
Y	mg COD/mg N	0.176	0.06	0.236	0.176	0.06	0.236
μ_m	day ⁻¹	1.270	0.081	1.255	1.08	0.19	–
b_A	day ⁻¹	0.03	0.03	–	0.054	0.054	–

Process characterization

Estimation of ASM parameters

To make the calibration easier, it is important to determine experimentally some of the parameters of the ASM. In this study, two tests were applied to determine (1) autotrophic max growth rate (μ_{A_NH} , $\mu_{A_NO_2}$), yields (Y_{A_NH} , $Y_{A_NO_2}$), decay rate (b_A) and half saturation substrate concentrations (K_{NH} and K_{NO_2}) of ammonium oxidizing bacteria X_{A_NH} and nitrite oxidizing bacteria $X_{A_NO_2}$ and (2) aerobic yield of heterotrophic biomass ($Y_{H_O_2}$).

The first was based on variable values of hydraulic retention time (HRT) and solid resident time (SRT) [22].

The values at 27.5°C were calculated for calibration and validation temperatures following formula [17]:

$$\mu_m(T^\circ\text{C}) = \mu_m(20^\circ\text{C}) \times \exp(\kappa(T - 20))$$

where κ is the temperature constant for μ_m and b_A .

The general results are given in Table 3.

The second type was made by respirometry. A procedure for the simultaneous characterization of carbon oxidation and nitrification was also proposed using an appropriate mixture of a readily biodegradable carbon source and NH_4^+ [28]. The value of $Y_{H_O_2}$ found is 0.67 day⁻¹.

Determination of sludge concentration and biomass fractionation

Non-settling particulate matter (f_{ns}) at the end of the cycle was estimated at 0.001 through SS measurement.

Ratio of active biomass was done on sludge samples at the beginning and the end of the calibration period. The total of ammonium and nitrite oxidizing bacteria was determined based on the total of species of Nitrosomonas, Nitrospira and Nitrobacter in nature [10]. Concentrations of these bacteria was determined as presented in Table 4, with volatile suspended solids (VSS) in the SBR estimated at the beginning and the end of the calibration to be 3 and 6.8 g/L, respectively.

Influent wastewater characterization

The influent wastewater characterization was done by referencing the STOWA protocol.

Table 4 Concentrations of ammonium and nitrite oxidizing bacteria

Stage	At the beginning of calibration	At the end of calibration
Bacteria	Concentration (g COD/L)	Concentration (g COD/L)
Nitrifying bacteria	0.403	1.49
X_{A_NH}	0.225	1.309
$X_{A_NO_2}$	0.194	0.147

Determining the organic matter (S_S , S_I , X_S , X_I) COD of the influent leachate was analyzed, which is equal to total COD.

The influent leachate was filtered with filter paper of 0.45 μm , the filtrated solution then was analyzed to get a COD which is equal to readily biodegradable organic (S_S) and inert soluble organic (S_I).

Ultimate BOD of the influent leachate was observed, which is equal to readily biodegradable organic (S_S) and slowly biodegradable organic (X_S).

Ultimate BOD of the filtrated influent leachate was observed, which is equal to readily biodegradable organic (S_S).

Determining the biomass components All biomass components including nitrifying bacteria (X_{A_NH} , $X_{A_NO_2}$), heterotrophic bacteria ($X_{H_NO_2}$, $X_{H_NO_3}$) as well as cell internal storage product of heterotrophic organisms (X_{STO}) were ignored.

Determining the nitrogen compounds The S_{NH} , S_{NO_2} and S_{NO_3} are obtained from ammonium, nitrite and nitrate measurements.

Calibration of the biokinetic model

Volume and flow rate simulation

First, parameters concerning to the volume, flow rate must be calculated exactly to have an exact evolution of volume and flow rate (Q_{in} , Q_{out} , Q_{waste} , etc.).

Nitrogen removal process simulation

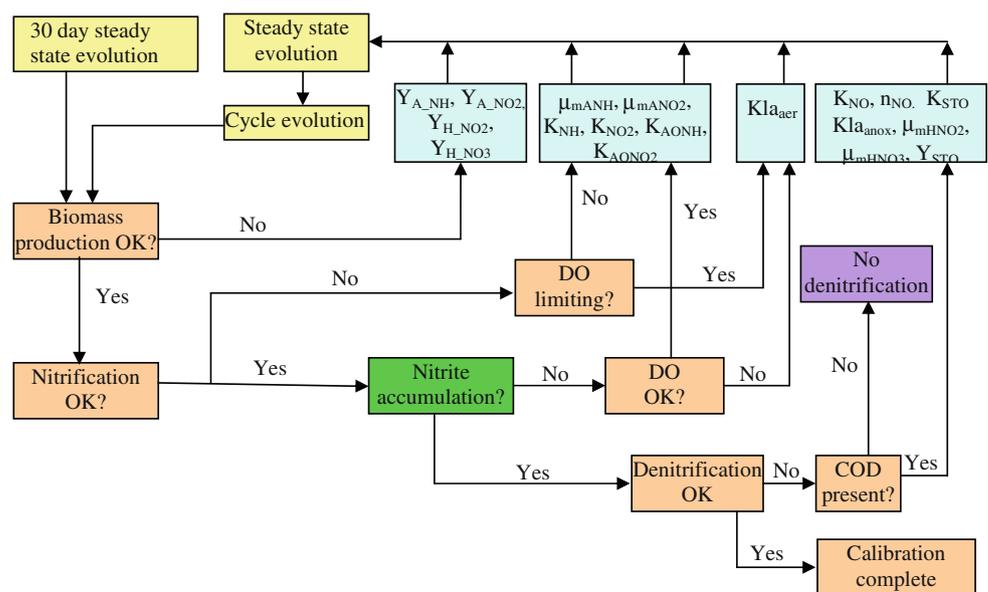
A simulation and an experiment of 30 days were performed to get a steady state. At the end of this period, the

cycle evolution was observed with a number of samples taken during the whole cycle. The values of parameters related to the dynamic behavior could be fitted. The kinetic and stoichiometric parameters (μ_{A_NH} , Y_{A_NH} , $Y_{A_NO_2}$, $Y_{H_O_2}$, b_A , K_{A_NH}), determined from biokinetic and respirometry tests were used as default values. However, some default values of kinetic and stoichiometric parameters available in ASM3, and literature values for the ones added in the ASM3_2step, were kept constant, while some others were adjusted step by step so that simulated analysed values fit with experimental ones. A procedure for the calibration of the biokinetic model was established, which combined BIOMATH (<http://biomath.ugent.be>) and STOWA (<http://www.stowa.nl>) procedures. This consisted in a step-wise methodology, which differentiated between the steady state calibration and the cycle (dynamic) evolution calibration. It was based on expert knowledge and consisted of five interaction steps that considered the sludge production, dynamics of DO, NH_4^+ , NO_2^- and NO_3^- . Figure 2 shows the methodology used for calibration.

1. Values of parameters found from measurements and biokinetic tests were applied, including f_{ns} , μ_{A_NH} , $\mu_{A_NO_2}$, Y_{A_NH} , $Y_{A_NO_2}$, K_{NH} .
2. Values of f_{S1} , f_{X1} , i_{N_S1} , i_{N_X1} , i_{N_X5} , i_{N_BM} , i_{TS_X5} , i_{TS_BM} , i_{TS_STO} and F_{BOD_COD} were kept constant as default values of the model.
3. Biomass production: simulated concentrations of ammonium and nitrite oxidizing bacteria at the beginning and at the end of the calibration period were compared to experimental values. Y_{A_NH} and $Y_{A_NO_2}$ were finally adjusted to 0.159 and 0.083 to fit the two

4. Nitrification profile: K_{la} of aeration phase was adjusted to increase little by little to obtain a reasonable nitrification profile. Nitrification includes ammonium trends, nitrite trends, nitrate trends and DO trends. It was necessary to set a K_{la} of aeration phase of 19.79 day^{-1} at the first day of steady state so that ammonium was consumed completely, to yield an ammonium removal efficiency corresponding to the experiment (the day when the 100% efficiency was obtained in both cases is the 21st) (Figs. 3, 4). K_{la} of the last day of calibration was obtained at 25.18 day^{-1} .
 5. Nitrite accumulation: to get a simulation similar to observed values, μ_{mANO_2} , K_{NO_2} , K_{AONH} , K_{AONO_2} parameters were gradually fine-tuned. Firstly, μ_{mANO_2} was decreased from a literature value of $0.7\text{--}0.32 \text{ day}^{-1}$. Ammonium uptake rates achieved during calibration and validation periods were 33.3 and 56.7 mg N/L h (with an ammonium removal efficiency of 100%), respectively, and nitrite accumulation ratios in the two periods were 91.4 and 95.6%, respectively. Those simulated values fit well with the experimental ones (not shown).
- It can be noticed that the increase of K_{la} does not negatively affect nitrite accumulation significantly. Here, the key parameter to yield a high nitrite to total of nitrite and nitrate ratio is the maximum specific growth rate of ammonium, and especially nitrite oxidizing bacteria. An appropriate nitrite accumulation can be obtained when the former growth rate was enough greater than the latter (e.g. 0.61 day^{-1}

Fig. 2 Partial nitrogen removal with two-step nitrification/denitrification calibration procedure



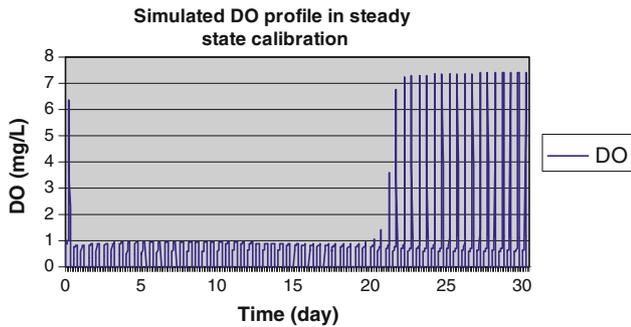


Fig. 3 DO profile at steady state

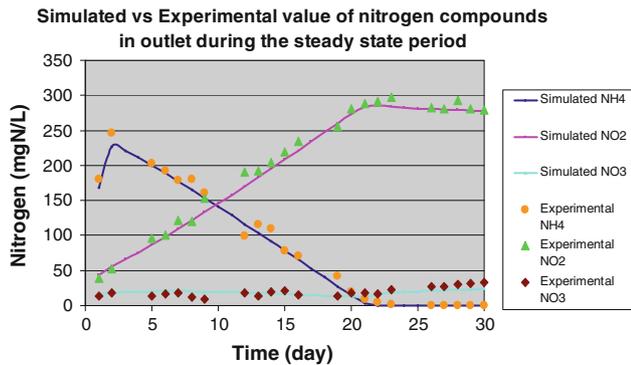


Fig. 4 Nitrogen profile at steady state

compared to 0.32), which signifies that nitrite oxidizing bacteria are inhibited. Here the inhibition factors are high pH, and alkalinity [2, 22].

- Cycle calibration: μ_{mANO_2} had to be decreased to 0.108 day^{-1} .

K_{AO_NH} and $K_{AO_NO_2}$ were fine-tuned from literature values of 0.5 and 1 mg O_2/L to 1.37 and 1.59 mg O_2/L , respectively, to better take into account the limiting effect of oxygen (Figs. 5, 6).

- Denitrification: when the nitrification profile and nitrite accumulation were correctly simulated the calibration was tuned for denitrification. As the system is not closed completely and observed DO values are not exactly zero but close to 0.05–0.1 mg/L, a K_{la_anox} of 0.1 h^{-1} was adopted.

Nitrite and nitrate denitrification rate depend on μ_{HNO_2} , μ_{HNO_3} , n_{NO} , K_{NO} . The most important substrate in denitrification is biodegradable COD which is very low in old leachate, and moreover has been degraded in the preceding nitrification process, or even stored partly in the biomass cells (in the form of X_{STO}), then has been liberated and combined with COD produced from biomass decay. The denitrification in this case, therefore, could be called endogenous denitrification.

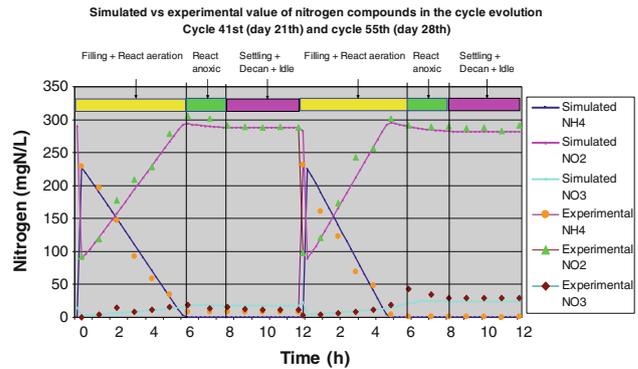


Fig. 5 Nitrogen profile in cycles 41 and 55

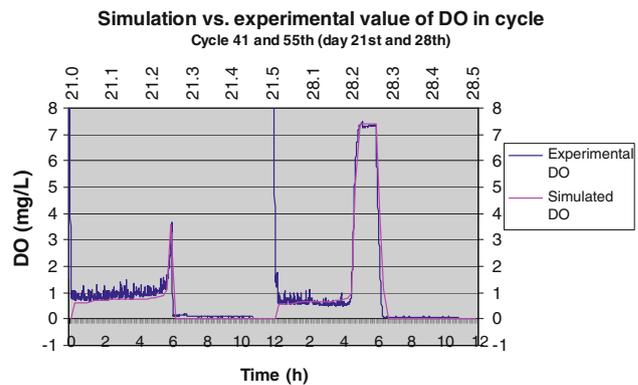


Fig. 6 DO profile in cycles 41 and 55

This COD participates into denitrification. The denitrification rate, therefore, also depends on k_{STO} , Y_{STO_NO} and $Y_{STO_O_2}$.

$Y_{STO_O_2}$ was increased from literature values of 8.5–0.87 to increase storage capability of COD in the biomass cells in the aeration phase, saving more COD for the denitrification process; then Y_{STO_NO} was decreased from 0.8 to 0.43 to reduce storage capability of COD in biomass cells in the anoxic phase.

Varying μ_{HNO_2} and μ_{HNO_3} does not change the nitrite and nitrate removal efficiency very much. These values, therefore, were kept constant and could be adjusted in a further step when simulating biomass production. At the same time, adjustment of K_{NO} and K_{STO} did not change denitrification efficiency significantly. It was found that, in the experiment, nitrite and nitrate denitrification efficiency with biodegradable COD in the influent leachate was low. Then, n_{NO} (0.6) was increased to the maximum value (1) and k_{STO} was adjusted from default value of the model of 5–3.2 to make nitrite and nitrate denitrification efficiency fit with the experiment.

Validation

The validation process consists in using the calibrated model with a set of data that is different from the calibration set. In this period, a 10-day simulation was run applying some operating changes and taking into account the influent variability. The composition of influent was presented above. Instead of the 7 l—maximum working volume, the 6 l—one was applied in this period with the same DO. K_{la} values of the filling-aerated as well as the aerated react phases, however, were changed since working volume was changed. Normally, there was no change in the kinetic and stoichiometric parameters. But temperature in this period was increased significantly (from 20.2 to 24.98°C) so the parameters most affected by temperature, including maximum specific growth rate (μ_A), decay constant (b_A), oxygen saturation K_{AO} of ammonium and nitrite oxidizing bacteria were increased according to the given temperature.

Figures 7 and 8 present results obtained from cycle measurements (9th day) in the validation period, showing a good fit between the simulated and experimental values for the oxygen and nitrogen compounds.

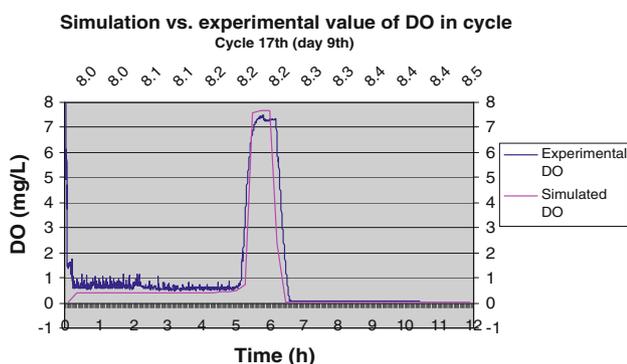


Fig. 7 Oxygen profile in cycles 17 and 19

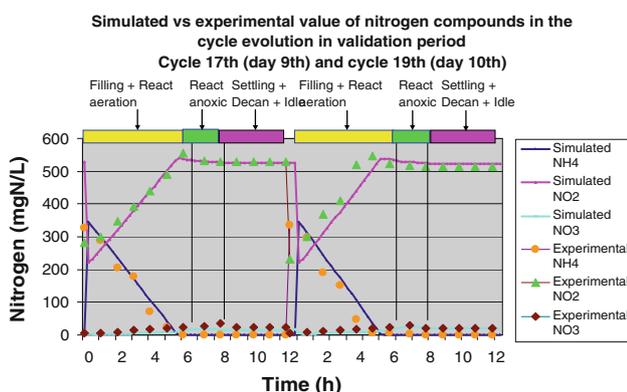


Fig. 8 Nitrogen profile in cycles 17 and 19

In Table 5, kinetic, stoichiometric and K_{la} values obtained during calibration and validation are presented. The * signifies values that varied with temperature.

Evaluation

The average relative deviation (ARD) of ammonium, nitrite and nitrate profiles between the simulation and the experiment calculated by Eq. 1 [25] are:

$$ARD = \frac{1}{n} \sum_{i=1}^n \left(\frac{|X_{i,exp} - X_{i,sim}|}{X_{i,exp}} \right) \tag{1}$$

where $X_{i,exp}$ and $X_{i,sim}$ are experimental and simulated values, respectively.

The ARD of NH_4^+ -N, NO_2^- -N and NO_3^- -N concentrations during calibration are 14.5, 3.6 and 18.5% and for validation 19.8, 6.2 and 22.3%, respectively.

Notably, the smaller ARD, the better fitting. Some values of ARD of NH_4^+ are not so good, the reason is that when the value of the NH_4^+ concentration is small (i.e., at the end of the nitrification process), only a small difference between the two sets of data can cause a large ARD, leading to a high ARD for the whole process. If we take into account error of sample analysis and we take values of the concentrations above ten, the ARDs are much smaller. The ARDs of nitrite in case of no carbon addition are always good since the value of the nitrite concentration in the whole cycle is high. The evaluation through the ARD, therefore, is relative; the results of the calibration and validation should be based on the evolution of whole process.

Further fittings will be done, but we consider that these results can be used to simulate the system to optimize the process.

Conclusion

Based on an appropriate model base, simulation and modeling of the partial nitrification and denitrification in the activated sludge—SBR treating leachate was successful. However, the temperature change during the experimental period hampered the calibration and, even more, the validation of model parameters. Using biokinetic tests to determine some kinetic and stoichiometric parameters, especially specific growth rates, improve robustness. The simulation of nitrogen profiles (carbon profiles are not presented in this paper) according to the experiment is successful, particularly the nitrite profile.

The activated sludge used for the study expressed its high nitrification capability with the presence of nitrifying bacteria, mostly due to the increase of the ammonium oxidizing bacteria. The studied leachate is characterized by

Table 5 Kinetic, stoichiometric and K_{la} values of calibration and validation period

Parameters	Unit	Default ASM3 model	Literature [15, 17] (20°C)	This study ASM3_2step	
				Calibration (20.2°C)	Validation (24.98°C)*
$b_{A_O_2}$	day ⁻¹	0.15	0.03	0.03	0.049*
K_{A_NH}	mg N/L		0.5	1.32	1.32
$K_{A_NO_2}$	mg N/L		1	1	1
$K_{A_O_NH}$	mg O ₂ /L		0.75	1.37	1.76*
$K_{A_O_NO_2}$	mg O ₂ /L		1	1.59	1.97*
k_{STO}	day ⁻¹	5		1.2	1.2
K_{STO}	mg COD/L	1		1	1
μ_{A_NH}	day ⁻¹		0.6	0.61	0.987*
$\mu_{A_NO_2}$	day ⁻¹		0.7	0.108	0.17*
$\mu_{H_NO_2}$	day ⁻¹		4.5	4.5	4.5
$\mu_{H_NO_3}$	day ⁻¹		4.5	4.5	4.5
n_{NO}	–	0.6		1	1
S_{O_Sat}	mg O ₂ /L	7		8.5	8
Y_{A_NH}	mg COD/mg N		0.1562	0.159	0.159
$Y_{A_NO_2}$	mg COD/mg N		0.085	0.083	0.083
$Y_{H_NO_2}$	mg COD/mg COD		0.54	0.54	0.54
$Y_{H_NO_3}$	mg COD/mg COD		0.54	0.54	0.54
$Y_{H_O_2}$	mg COD/mg COD	0.63		0.67	0.67
Y_{STO_NO}	mg COD/mg COD	0.8		0.43	0.43
$Y_{STO_O_2}$	mg COD/mg COD	0.85		0.87	0.87
K_{la} react 1 end	h ⁻¹	–	–	25.18	33.5*

high pH and alkalinity, causing inhibition of nitrite oxidizing bacteria. Dissolved oxygen showed its influence (negatively) only in nitrite accumulation at the end of the cycle at steady state, when ammonium is completely consumed and alkalinity remains low. This caused a decrease in pH, activating the nitrite oxidizing bacteria strongly again. However, the duration of this period is not long, thus total nitrite accumulation remains very high, at 91.4 and 95.6% in the calibration and validation periods, respectively. Optimization of the partial nitrification and improvement of nitrogen removal efficiency will be continued in a future study by adjusting DO, HRT (working volume of SBR) and cycles (time for each phase). The developed model as well as the kinetic, stoichiometric parameters calibrated will be used to optimize the process, and the optimized system will be checked by new experiments.

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