Modelling biological nitrogen and phosphorus removal with soluble microbial products (SMP) production-degradation processes

Alida Cosenza[1], Giorgio Mannina[1], Marc B. Neumann[2], Gaspare Viviani[1] and Peter A. Vanrolleghem[2]

1) Dipartimento di Ingegneria Civile, Ambientale e Aerospaziale, Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy (E-mail: cosenza@idra.unipa.it, mannina@idra.unipa.it, gviv@idra.unipa.it)
2) model*EAU*, Département de génie civil et de génie des eaux, Université Laval, 1065 av. de la Médecine, Québec (QC) G1V 0A6, Canada (E-mail: Marc.Neumann@gci.ulaval.ca, Peter.Vanrolleghem@gci.ulaval.ca)

Abstract
Over the last two decades, Membrane Bioreactors (MBR) are increasingly used for wastewater treatment. Mathematical modelling of MBR systems has played a key role in order to better explain the effect of their peculiarities. Indeed, several MBR models have been presented in literature in order to improve the knowledge on MBR systems: biological models, hybrid models which include soluble microbial product (SMP) modelling, physical models able to describe the membrane fouling and integrated models which couple the hybrid models with the physical ones.
However, among the existing MBR models only few integrated models have been developed which take into account the existing relationship between fouling and the biological processes. Also, with respect to modelling of biological phosphorus removal in MBR systems, due to the complexity of the process, practical use of the models is still limited. There is a vast knowledge (and consequently a vast amount of data) on nutrient removal for conventional activated sludge (CAS) systems but only limited information on phosphorus removal for MBRs. Moreover, calibration of these complex integrated models still remains the main bottleneck to their employment.
The paper presents an integrated mathematical model able to simultaneously describe biological nutrient removal, the SMP formation/degradation and the physical removal of organics. The model has been calibrated by using data collected in a UCT-MBR pilot plant, built at the Palermo WWTP and fed with real wastewater, applying an innovative calibration protocol. The calibrated model provides acceptable correspondence with experimental data.

Keywords
ASM2d-SMP; MBR modelling; membrane fouling; model calibration; nitrogen phosphorus removal.

Introduction

In the last decade the use of membrane bioreactor (MBR) technology, for municipal as well as industrial wastewater, has increased significantly thanks to its technological advantages and decreasing membrane costs. At the same time, the need to improve the MBR process understanding, design and operation has grown. The peculiarities of MBR systems such as the solid liquid separation, the high suspended solids concentration and the high sludge retention times (SRT) induce big differences in the sludge properties and dynamic behaviour of MBR systems compared to the well-known conventional activated sludge (CAS) systems (Jiang *et al*., 2009; Di Trapani *et al*., 2011). These differences have been experimentally studied by several authors which fundamentally highlighted the greater stability of the autotrophic biomass activity in MBR systems than in CAS (among others Munz *et al*., 2008). Moreover, several MBR models have been presented in literature in order to better explain the effect of the peculiarities of the MBR. In particular, as discussed by Fenu *et al*. (2010), the activated sludge models (ASMs), originally developed for CAS systems, have been applied in their original form or adapted in order to simulate

MBR systems (among others, Jiang *et al*., 2008; Spérandio and Espinosa, 2008; Mannina *et al*., 2010). MBR modelling literature gives particular attention to membrane fouling by introducing "integrated" models (Ng and Kim, 2007) which basically couple the biological model (including the soluble microbial products (SMPs) formation/degradation processes according to the "hybrid" configuration models) with the physical models (Lee *et al*., 2002; Di Bella *et al*., 2008; Zarragoitia-González *et al*., 2008). Among the published integrated models only few models take into account the existing relationship between the removal effect of the reversible fouling (cake layer) and the biological processes. Among these, the model proposed by Di Bella *et al*. (2008) is able to describe, for a single MBR reactor, the effect of the cake layer on COD removal according to the deep bed theory (Kuberkar and Davis, 2000).
Nevertheless, integrated MBR models able to describe the biological nutrient removal (BNR) processes as well as SMP formation/degradation and physical separations are not yet fully available. Indeed, in the wide MBR modelling literature overview provided by Fenu *et al*. (2010) the need for further studies on MBR phosphorus removal and on SMPs transport through the membrane is underlined. In fact, knowledge concerning the influence of the MBR sludge properties on biological phosphorus removal process, though studied by different authors, is still limited (among others Monclùs *et al*., 2010; Zhang *et al*., 2009). Moreover, the existing integrated models, which introduce new processes (e.g. SMP formation/degradation and physical processes), variables and parameters, are complex and generally characterized by several parameters that need to be quantified in view of the frequent lack of data. The calibration of these models, still remains the weakest link in their employment (Hauduc *et al*., 2009).
This paper proposes an integrated mathematical model able to describe nitrification, denitrification, biological phosphorus removal and SMP formation/degradation which occur in a UCT-MBR system according to Jiang *et al*. (2008) and the influence of the cake layer in the COD removal according to Di Bella *et al*. (2008). An innovative calibration protocol proposed by Mannina *et al*. (in press) is also applied to estimate the model parameter values by using the data collected in an UCT-MBR pilot plant fed with real wastewater.

Methods

Model description

The MBR model is divided into two sub-models: a biological and a physical sub-model. It involves 19 biological state variables and 79 parameters (kinetics, stoichiometry, physical parameters and fractionation coefficients). The proposed integrated MBR model couples the ASM2d-SMP model first introduced by Jiang *et al*. (2008) with a physical sub-model derived from Mannina *et al*. (2010) and Di Bella *et al*. (2008).
The biological sub-model is a modified version of ASM2d (Jiang *et al*., 2008) and takes into account two new state variables, S_{UAP} (soluble utilization associated product) and S_{BAP} (soluble biomass associated product), and six new processes (anaerobic, aerobic and anoxic hydrolysis of both UAP and BAP). The sum of S_{UAP} and S_{BAP} is equal to the modelled SMP. According to Jiang *et al*. (2008) S_{UAP} and S_{BAP} are both defined to have a size < 0.45 μm, to be produced in the system and to be biodegradable.
The assumptions, processes and variables of ASM2d are still valid except for the process (and related variables) of phosphorus precipitation that has been neglected; for the variables and process descriptions refer to ASM2d (Henze *et al*., 2000). The S_{BAP} production is described to be proportional to the biomass decay and is characterised by the stoichiometric parameter f_{BAP} (fraction of BAP generated per biomass decayed). The S_{BAP} reduction which is due to aerobic, anoxic and anaerobic hydrolysis processes following saturation kinetics is characterised by the hydrolysis rate coefficient for S_{BAP} ($k_{H,BAP}$). The S_{UAP} production and degradation are similarly described by introducing the coefficients f_{UAP} (fraction of UAP generated in biomass decay) and $k_{H,BAP}$.

The total COD (COD_{TOT}), total soluble COD (COD_{SOL}), total phosphorus (TP), total nitrogen (TN) and mixed liquor suspended solid (MLSS) are described as follows, where the coefficients in the Eqs.1-5 are defined according to ASM2d:

$$COD_{TOT} = S_F + S_A + S_I + S_{UAP} + S_{BAP} + X_I + X_S + X_H + X_{AUT} + X_{PAO} + X_{PHA} \quad (1)$$

$$COD_{SOL} = S_F + S_A + S_I + S_{UAP} + S_{BAP} \quad (2)$$

$$TP = S_{PO4} + i_{PSF} \cdot S_F + i_{PSI} S_I + i_{PXS} \cdot X_S + i_{PXI} \cdot X_I + i_{PBM} \cdot \left(X_H + X_{AUT} + X_{PAO}\right) \quad (3)$$

$$TN = S_{NO3} + S_{NH4} + i_{NSF} \cdot S_F + i_{NSI} S_I + i_{NXS} \cdot X + i_{NXI} \cdot X_I + i_{NBM} \cdot \left(X_H + X_{AUT} + X_{PAO}\right) \quad (4)$$

$$MLSS = i_{TSS,XI} \cdot X_I + i_{TSS,XS} \cdot X_S + i_{TSS,BM} \cdot \left(X_H + X_{AUT} + X_{PAO}\right) + i_{TSS,XPP} \cdot X_{PP} + i_{TSS,XPHA} X_{PHA} \quad (5)$$

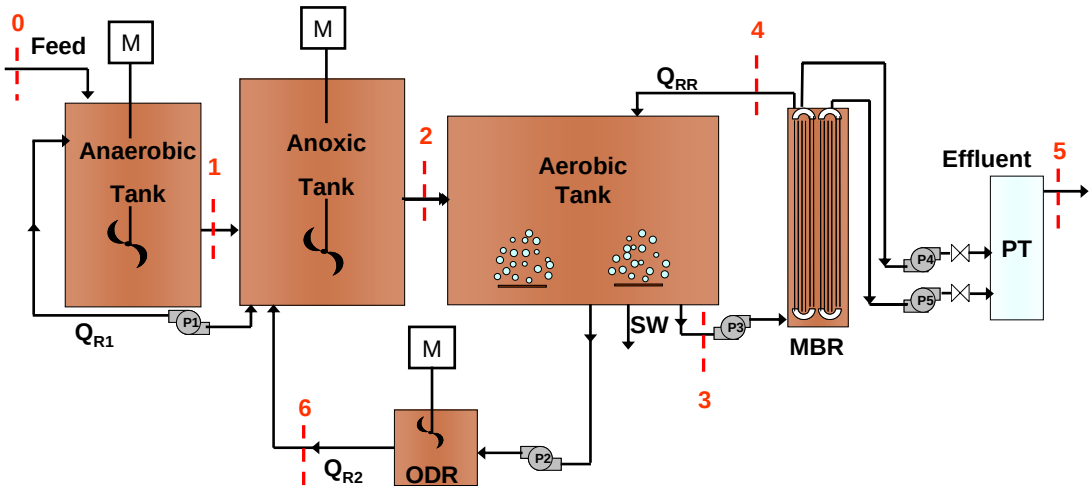
The physical sub-model is derived by an integrated MBR model developed in previous studies (Di Bella *et al*., 2008; Mannina *et al*., 2010). The model describes the cake layer formation during the suction and backwashing phases and the partial COD removal throughout the cake layer, taking into account the reversible fouling of the membrane. In particular, according to the model proposed by Li and Wang (2006) and the application proposed by Di Bella *et al*. (2008) the rate of sludge attachment and detachment on the membrane surface are modelled continuously throughout the suction backwashing phase, making it possible to evaluate the solid mass deposited on the membrane surface and the cake layer thickness, δ(t) at any time (see Di Bella *et al*., 2008). Subsequently, by applying the deep-bed theory (Bai and Tien, 2000; Kuberkar and Davis, 2000) with the approach of Jang *et al*. (2006) the physical sub-model is able to describe the COD profile across the biological membrane represented by the cake layer. A fraction of particles is retained inside the cake layer and the COD_{TOT} on the cake layer outer surface (which represents the output of the biological model) is reduced across the membrane before the physical filtration. Finally, the model describes the total physical and biological contribution to COD_{TOT} removal which depends on the fraction of particles removed by the bed (according to the deep bed theory) and on the fraction of particles retained by the physical membrane. The link between the two sub-models is represented by the MLSS concentration in the MBR reactor.

Data collected during the sampling campaign were used to compose a continuous input series generated from the discrete input measured data by employing a Fourier series (Mannina *et al*., in press).

Pilot plant and sampling campaign description

The model was applied and calibrated to a UCT-MBR pilot plant, Figure 1, located at the Acqua dei Corsari (Palermo) wastewater treatment plant (WWTP). It consisted of three reactors in series, anaerobic (mean volume 72 L), anoxic (mean volume 165 L) and aerobic (mean volume 327 L) respectively, followed by an aerobic container (mean volume 52 L) where two submerged hollow fibre membrane modules (Zenon Zeeweed, ZW 10) were installed. The presence of the oxygen depletion reactor (ODR) ensures anoxic conditions in the second reactor despite the intensive aeration in the aerobic tank. Each membrane module was characterized by a pore size of 0.04 μm and a nominal surface of 0.93 m^2. The pilot plant was fed with 40 L/h (Q_{FEED}) of municipal wastewater. The permeate was extracted using an ad-hoc permeate extraction pump (for each membrane) by imposing an average flux of 42 $Lm^{-2}h^{-1}$ on the membrane surface and a maximum depression (which occurs during the extraction period) of -0.50 bar. The membranes were periodically subjected to physical and chemical cleaning. Chemical cleaning was conducted by using a solution of 2 g/L of citric acid in order to reduce the trans-membrane pressure. The plant was operated for 165 days. Until day 76 it was operated with complete sludge retention while after day 76, the sludge was regularly withdrawn, maintaining the sludge age near 37 days. The average mixed liquor suspended solids (MLSS) concentrations ranged from 3 to 6.5 gTSS/l with an average percentage of volatile fraction of 70% and an average value of the Food/Microorganism ratio (F/M) equal to 0.13 $kgTCOD \cdot kgVSS^{-1}\ d^{-1}$.

During the entire period the composite influent wastewater (section 0), the grab mixed liquor in each tank (sections 1-4), the mixed liquor in ODR (section 6) and the permeate (section 5) were sampled three times per week and analysed for total and volatile suspended solids (TSS and VSS), total and soluble COD, NH_4-N, NO_2-N, NO_3-N, N_{TOT}, P_{TOT} (APHA, 1998). Moreover, daily measurements in each section were conducted for dissolved oxygen (DO), pH and temperature (T) using a handheld Multi-meter 340i (WTW). A physical-chemical characterization of the influent was performed analysing COD, NH_4-N, NO_2-N, NO_3-N, N_{TOT} and P_{TOT} from influent grab samples withdrawn at hourly intervals during 24 hours. Further details about the pilot plant and the sampling campaign can be found in literature (Di Trapani *et al.*, 2011).



LEGEND			
M	Mixer	QR1-QR2	Mixed Liquor Recycle
PT	Permeate tank	RR	Retained Recycle
P1-P2- P3	Pump of the mixed liquor recycle	SW	Sludge wasting
P4- P5	Permeate extraction pump	⊠	Bidirectional valve
ODR	Oxygen Depletion Reactor	- - -	Sampling point

Figure 1. Schematic overview of the UCT-MBR pilot plant

Sensitivity analysis and model calibration

Sensitivity analysis represents a very powerful tool, as it is able to provide information about how the variation in the output of the model can be apportioned to the variation of the input factors (Saltelli, 2000). In the case of an over-parameterised model it may be performed in order to select the region in the space of input factors (i.e. parameters) on which to focus the attention during the model calibration (Saltelli, 2004). In this work a previous screening of the most influential kinetic, stoichiometric and fractionation model parameters by means of a preliminary global sensitivity analysis (GSA) has been performed (Cosenza *et al.*, 2011). In particular, the results of the application of the Standardized Regression Coefficients (SRC) method have been used. The SRC method consists of running a Monte Carlo simulation (with random sampling of input factors) and performing a multivariate linear regression between the model output and the input factors. The SRC's (β_i), which represent the standardised regression slopes of the regression, are valid measures of sensitivity when, as suggested by Saltelli (2004), the coefficient of determination R^2 is greater than 0.7.. After a preliminary trial and error calibration, the parameter values have been estimated by applying an innovative calibration protocol developed in previous studies (Mannina *et al.*, in press). This protocol employs a novel step-wise Monte Carlo based calibration of the subset of influential parameters. The speciality of this procedure is that different subsets of model parameters corresponding to sub-groups of model outputs are differentiated. In this way the combination of issues connected to the model complexity, the lack of data and the large number of parameters involved are tackled. The calibration protocol simplifies the problem of finding the optimal parameter set by splitting the estimation task in steps. A preliminary global sensitivity analysis is carried out in order to identify the most influential model parameters to be calibrated for each model

output sub-group. The sub-groups of model outputs and corresponding influential parameters to be calibrated are then selected and the iterative step-wise procedure is applied considering a specific calibration order (defined either according to the modeller's experience or in an objective way) of these output sub-groups.

In order to quantify how the variation of the influential model parameters influences the model output (Y) and which set represents the best calibrated set, the expression for the likelihood (Eq. 6) and global model efficiency (Eq. 7) used by Mannina *et al*. (in press) were used:

$$L\left(\theta_i / Y_j\right) = \exp\left(\frac{-\sigma^2_{Mj-Oj}}{\sigma^2_{Oj}}\right) \quad (6)$$

where θ_I, represents the *ith* set of (randomly generated) model parameters, $\sigma^2_{Mj\text{-}Oj}$ represents the sum of squared errors between model output ($M_{j,i}$) and observation ($O_{j,i}$) of the *jth* variable, while σ^2_{Oj} is the sum of squared errors between the observations ($O_{j,i}$) and the average value of the observations ($\overline{O}_j$) for the period under consideration.

$$E_i = \sum_j^n \alpha_j L\left(\theta_i / Y_j\right) \quad (7)$$

where E_i represents the weighted sum of the likelihood measures of the *n* model outputs computed on the *ith* selected parameter set (θ_i) and α_j is a normalizing constant that represents the weight of the *jth* model output.

All algorithms were coded in Fortran. Simulations were performed with an ASUS AMD Athlon 64 X2 Dual Core Processor 4000+, 2.1 GHz, with 2GB ram memory. One model simulation requires approximately 3 minutes.

Results and discussion

Preliminary Sensitivity analysis

The SRC method was applied considering the broadest variation range for each model parameter found in the relevant literature (among others Hauduc *et al*., 2011; Brun *et al*., 2002; Weijers and Vanrolleghem, 1997). A parameter matrix (800×79) was generated using Latin hypercube sampling (LHS). Monte Carlo simulation was performed on the sampled parameter values. As in Sin *et al*. (2011), abs(β_i) with values above 0.1 were selected as being influential. For each of the chosen pilot plant sections (1-5) and for each of the 21 model state variables, a set of influential model parameters has been selected by applying the SRC method. In particular, for each chosen plant section, the time-averaged state variables were considered. Therefore, 21 sensitivity coefficients have been calculated for each model parameter. Table 2 summarizes the results of the sensitivity analysis for each sub-group of model outputs.

Table 2. Synthesis on the results of the preliminary sensitivity analysis: sub-groups of model outputs; model outputs taken into account during the analysis, calibration order, influential model parameters for each sub-group and performed Monte Carlo (MC) runs for the model calibration

Sub-group	Model output	Calibration order	Influential parameters sub-group	MC runs
P	$S_{PO,1}$, $S_{PO,2}$, $S_{PO,3}$, $S_{PO,5}$	**I**	k_H, η_{FE}, K_{NO3}, μ_H, b_H, q_{PHA}, q_{PP}, μ_{PAO}, b_{PAO}, Y_H, f_{XI}, Y_{PAO}, $i_{P,XI}$, $i_{P,XS}$, $i_{P,BM}$	9570
N	$S_{NH4,1}$, $S_{NO3,1}$, $S_{NH4,2}$, $S_{NO3,2}$, $S_{NH4,3}$, $S_{NO3,3}$, $TN_{,5}$, $S_{NH4,5}$, $S_{NO3,5}$	**II**	k_H, K_O, μ_H, $\eta_{NO3,H}$, b_H, $K_{NH,H}$, μ_{AUT}, Y_H, f_{XI}, F_{SA}, f, $i_{N,XI}$, $i_{N,XS}$	3444
COD	$COD_{TOT,1}$, $COD_{TOT,2}$, $COD_{TOT,3}$, $COD_{SOL,3}$, $COD_{TOT,5}$	**III**	k_H, μ_H, b_H, $K_{NH,H}$, μ_{AUT}, Y_H, β, f	3379
MLSS	MLSS,1, MLSS,2, MLSS,3	**IV**	k_H, μ_H, f_{XI}	3502

In particular, the MLSS, N, COD and P sub-groups of model outputs were considered; a model parameter is influential for a sub-group if it is classified as influential for at least one of the model outputs of that sub-group. Globally, 24 model parameters were classified as being influential. A substantial reduction (>65%) in the number of model parameters to calibrate was therefore accomplished. The model parameters classified as being influential present good consistency with the relevant processes occurring in each plant section. For example, one of the most influential parameters for $S_{PO,1}$ (orthophosphate in section 1) was q_{PHA} (rate constant for S_A uptake rate); this parameter is representative of the phosphorus release process which occurs in anaerobic conditions. The positive sign of the resulting value of β_i (β_i=0.32) for q_{PHA} indicates a positive effect on the $S_{PO,1}$ value. Another example is the influence of the parameters μ_H (maximum growth rate of heterotrophic organisms) and Y_H (yield coefficient for heterotrophic organisms growth) on the model output $S_{NO3,2}$ with β_i respectively equal to -0.32 and 0.22.
Once the influential model parameters have been selected, for each sub-group, the calibration order was defined (Table 2). For each selected model output the sum of the absolute values of β_i for the influential model parameters has been computed first. Thereafter, the average sum of the β_i of each sub-group (β_M) has been calculated. The order of the different calibration sub-groups has been established by ranking the calibration sub-group with respect to β_M. The model output sub-groups were ranked on the basis of the β_M values. The first calibration order has been assigned to the sub-group which presents the highest β_M value.

Calibration
Even though the calibration protocol doesn't include a preliminary manual calibration, the computational time of the automatic calibration, can be reduced by first performing a calibration by means of the trial and error method: according to the modeller's experience the default values (taken from literature) of some parameters have been changed in order to improve the simulated versus measured concentration profiles of the model outputs taken into account. The *a priori* set of model parameters is thus obtained from this trial and error calibration (Table 3). This set is equal to the default one except for the parameters f_{XI}, f_{BAP}, $i_{TSS,XI}$, $i_{TSS,XS}$, $i_{TSS,BM}$ and b_{AUT} which respectively represent the fraction of X_I generated in biomass decay, the fraction of BAP generated in biomass decay, the conversion factor X_I in TSS, the conversion factor X_S in TSS, the conversion factor biomass in TSS and the decay rate coefficient for autotrophic organisms. The parameters f_{XI} (default=0.1, *a priori*=0.05), f_{BAP} (default=0.022, *a priori*=0.007), $i_{TSS,XI}$ (default=0.75, *a priori*=0.7875), $i_{TSS,XS}$ (default=0.75, *a priori*=0.7875), $i_{TSS,BM}$ (default=0.9, *a priori*=0.945) were substantially changed in order to improve the fit between the simulated and measured MLSS values; the value of b_{AUT} (default=0.15 d^{-1}, a priori=0.08 d^{-1}) was reduced in order to improve the description of the nitrification process. The b_{AUT} value is in agreement with values found in literature for MBR systems (Di Trapani *et al*., 2011; Lubello *et al*., 2009).
Then, the influential model parameters of Table 2 were calibrated by applying the calibration protocol proposed by Mannina *et al*. (in press), based on the Generalized Likelihood Uncertainty Estimation (GLUE) methodology (Beven & Binley 1992), considering the model outputs of Table 2. For each sub-group, starting from the first sub-group (P) up till the last one (MLSS), several Monte Carlo runs were performed, each time varying only the influential parameters for this sub-group (non influential model parameters are maintained equal to their a priori value). The required number of MC runs (see Table 2) was different from sub-group to sub-group. Similarly to Mannina *et al.* (in press), this study was carried out by analyzing the model efficiency variations increasing the sample dimension from 100 to 10000 Monte Carlo simulations. The same parameter ranges as used in the preliminary sensitivity analysis were used (see Table 3) and no correlation between parameters was assumed.

Table 3. Values of model parameters (default, a priori and calibrated), variation ranges and literature references

Symbol	Unit	default	*a priori*	MIN	MAX	calibrated	Reference
k_H	g X_S.g X_H^{-1}.d^{-1}	3	3	1.5	4.5	1.7248	Brun et al., 2002
$\eta_{NO3,HYD}$	-	0.6	0.6	0.402	0.798	-	Hauduc et al., 2010
η_{FE}	-	0.4	0.4	0.2	0.6	0.4786	Hauduc et al., 2010
K_O	g S_{O2}.m^{-3}	0.2	0.2	0.1	1	0.5388	Weijers and Vanrolleghem, 1997
K_{NO3}	g S_{NO3}.m^{-3}	0.5	0.5	0.1	0.625	0.3157	Weijers and Vanrolleghem, 1997; Brun et al., 2002
K_X	g X_S.g X_H^{-1}	0.1	0.1	0.05	0.15	-	Brun et al., 2002
$K_{O,HYD}$	g S_{O2}.m^{-3}	0.2	0.2	0.1	0.3	-	Brun et al., 2002
$K_{NO3,HYD}$	g N.m^{-3}	0.5	0.5	0.375	0.625	-	Brun et al., 2002
μ_H	d^{-1}	6	6	0.6	13.2	1.3000	Jeppsson, 1996
q_{FE}	g S_F.g X_H^{-1}.d^{-1}	3	3	1.5	4.5	-	Brun et al., 2002
$\eta_{NO3,H}$	-	0.8	0.8	0.6	1	0.9852	Brun et al., 2002
b_H	d^{-1}	0.4	0.4	0.05	1.6	0.5829	Jeppsson, 1996
K_F	g S_F.m^{-3}	4	4	2	6	-	Brun et al., 2002
K_{FE}	g S_F.m^{-3}	4	4	2	6	-	Brun et al., 2002
K_A	g S_A.m^{-3}	4	4	2	6	-	Brun et al., 2002
$K_{NH,H}$	g S_{NH4}.m^{-3}	0.05	0.05	0.02	2	0.0953	Weijers and Vanrolleghem, 1997
K_P	g S_{PO4}.m^{-3}	0.01	0.01	0.005	0.015	-	Brun et al., 2002
$K_{ALK,H}$	mol HCO_3^-.m^{-3}	0.1	0.1	0.05	0.15	-	Brun et al., 2002
q_{PHA}	g X_{PHA}.g X_{PAO}^{-1}.d^{-1}	3	3	0.3	5.7	3.6991	Hauduc et al., 2010
q_{PP}	g X_{PP}.g X_{PAO}^{-1}.d^{-1}	1.5	1.5	0	3.3	2.3413	Hauduc et al., 2010
μ_{PAO}	d^{-1}	1	1	0.5	1.5	0.7167	Brun et al 2002
$\eta_{NO3,PAO}$	-	0.6	0.6	0.45	0.75	-	Brun et al., 2002
b_{PAO}	d^{-1}	0.2	0.2	0.1	0.25	0.2351	Henze et al., 2000;Hauduc et al., 2010
b_{PP}	d^{-1}	0.2	0.2	0.1	0.25	-	Henze et al., 2000;Hauduc et al., 2010
b_{PHA}	d^{-1}	0.2	0.2	0.1	0.25	-	Henze et al., 2000;Hauduc et al., 2010
K_{PS}	g S_{PO4}.m^{-3}	0.2	0.2	0.1	0.3	-	Brun et al., 2002
K_{PP}	g X_{PP}.g X_{PAO}^{-1}	0.01	0.01	0.005	0.015	-	Brun et al., 2002
K_{MAX}	g X_{PP}.g X_{PAO}^{-1}	0.34	0.34	0.2	0.51	-	Rieger et al., 2001
K_{IPP}	g X_{PP}.g X_{PAO}^{-1}	0.02	0.02	0.01	0.03	-	Brun et al., 2002
K_{PHA}	g X_{PHA}.g X_{PAO}^{-1}	0.01	0.01	0.005	0.015	-	Brun et al., 2002
$K_{O,PAO}$	g S_{O2}.m^{-3}	0.2	0.2	0.1	0.3	-	Brun et al., 2002
$K_{NO3,PAO}$	g S_{NO3}.m^{-3}	0.5	0.5	0.375	0.625	-	Brun et al., 2002
$K_{A,PAO}$	g S_A.m^{-3}	4	4	2	6	-	Brun et al., 2002
$K_{NH,PAO}$	g S_{NH4}.m^{-3}	0.05	0.05	0.025	0.075	-	Brun et al., 2002
$K_{P,PAO}$	g S_{PO4}.m^{-3}	0.01	0.01	0.005	0.015	-	Brun et al., 2002
$K_{ALK,PAO}$	mol HCO_3^-.m^{-3}	0.1	0.1	0.05	0.15	-	Brun et al., 2002
μ_{AUT}	d^{-1}	1	1	0.2	1.2	1.1810	Weijers and Vanrolleghem, 1997
b_{AUT}	d^{-1}	0.15	0.08	0.04	0.1605	-	Hauduc et al., 2010
$K_{O,A}$	g S_{O2}.m^{-3}	0.5	0.5	0.1	2	-	Weijers and Vanrolleghem, 1997; Jeppsson, 1996
$K_{NH,A}$	g S_{NH4}.m^{-3}	1	1	0.5	1.5	-	Hauduc et al., 2010

Symbol	Unit	default	*a priori*	MIN	MAX	calibrated	Reference
$K_{ALK,A}$	mol HCO_3^-.m^{-3}	0.5	0.5	0.25	0.75	-	Brun et al., 2002
$K_{P,A}$	g S_{PO4}.m^{-3}	0.01	0.01	0.005	0.015	-	Brun et al., 2002
$k_{H,BAP}$	d^{-1}	0.000000741	7.41E-07	3.71E-07	1.112E-06	-	Jiang et al., 2008
$k_{H,UAP}$	d^{-1}	0.0102	0.0102	0.0051	0.0153	-	Jiang et al., 2008
$k_{LaT,3}$	h^{-1}	10	10	9.5	10.5	-	Innocenti, 2005
$k_{LaT,4}$	h^{-1}	3.4	3.4	3.23	3.57	-	Innocenti, 2005
Y_H	g X_H.g X_S^{-1}	0.625	0.625	0.38	0.75	0.3913	Jeppsson, 1996
f_{XI}	g X_I.g X_H^{-1}	0.1	0.05	0.05	0.4	0.0600	Weijers and Vanrolleghem, 1997
Y_{PAO}	g X_{PAO}.g X_{PHA}^{-1}	0.625	0.625	0.42	0.78125	0.4428	Brun et al., 2002
Y_{PO4}		0.4	0.4	0.38	0.42	-	Brun et al., 2002
Y_{PHA}	g X_{PP}.g X_{PHA}^{-1}	0.2	0.2	0.19	0.21	-	Brun et al., 2002
Y_A	g X_{PP}.g X_{PHA}^{-1}	0.24	0.24	0.228	0.252	-	Brun et al., 2002
f_{BAP}	-	0.0215	0.007	0.0069	0.022575	-	Brun et al., 2002
f_{UAP}	-	0.0963	0.0963	0.091485	0.101115	-	Brun et al., 2002
F_{SF}	-	0.12	0.12	0.06	0.18	-	Brun et al., 2002
F_{SA}	-	0.08	0.08	0.04	0.12	0.0425	Brun et al., 2002
F_{SI}	-	0.12	0.12	0.114	0.126	-	Brun et al., 2002
F_{XI}	-	0.1	0.1	0.05	0.15	-	Brun et al., 2002
F_{XH}	-	0.1	0.1	0.06	0.18	-	Brun et al., 2002
β	-	0.01234509	0.01234509	1.00E-04	2.10E-02	0.0138	Di Bella et al.,2008
α	-	0.47773695	0.47773695	0	1	-	Di Bella et al.,2008
γ	Kg m^{-3} s	0.00242427	0.00242427	5.56E-04	2.78E-03	-	Di Bella et al.,2008
f	-	0.18	0.18	0.001	0.99	0.9104	Di Bella et al.,2008
λ	m^{-1}	1520.291091	1520.29109	1000	2.00E+03	-	Di Bella et al.,2008
C_E	-	0.99794265	0.99794265	0.996	0.999	-	Di Bella et al.,2008
$i_{N,SI}$	g N.g S_I^{-1}	0.01	0.01	0.0075	0.0125	-	Brun et al., 2002
$i_{N,SF}$	g N.g S_F^{-1}	0.03	0.03	0.0225	0.0375	-	Brun et al., 2002
$i_{N,XI}$	g N.g X_I^{-1}	0.02	0.02	0.015	0.025	0.0245	Brun et al., 2002
$i_{N,XS}$	g N.g X_S^{-1}	0.04	0.04	0.03	0.05	0.0437	Brun et al., 2002
$i_{N,BM}$	g N.g X_{BM}^{-1}	0.07	0.07	0.0665	0.0735	-	Brun et al., 2002
$i_{P,SF}$	g P.g S_F^{-1}	0.01	0.01	0.005	0.015	-	Brun et al., 2002
$i_{P,XI}$	g P.g X_I^{-1}	0.01	0.01	0.005	0.015	0.0056	Brun et al., 2002
$i_{P,XS}$	g P.g X_S^{-1}	0.01	0.01	0.005	0.015	0.0099	Brun et al., 2002
$i_{P,BM}$	g P.g X_{BM}^{-1}	0.02	0.02	0.015	0.025	0.0207	Brun et al., 2002
$i_{TSS,XI}$	g TSS.g X_I^{-1}	0.75	0.7875	0.7125	0.7875	-	Brun et al., 2002
$i_{TSS,XS}$	g TSS.g X_S^{-1}	0.75	0.7875	0.7125	0.7875	-	Brun et al., 2002
$i_{TSS,BM}$	g TSS.g X_{BM}^{-1}	0.9	0.945	0.855	0.945	-	Brun et al., 2002
$i_{TSS,XPHA}$	g TSS.g X_{PHA}^{-1}	0.6	0.6	0.57	0.63	-	Brun et al., 2002
$i_{TSS,XPP}$	g TSS.g X_{PP}^{-1}	3.23	3.23	3.0685	3.3915	-	Brun et al., 2002

For each run, simulated outputs were compared with measured data computing the model output efficiency according to Equation 6. For each sub-group the calibrated set of parameters, corresponding to the maximum value of the global model efficiency (Eq. 7) was selected. The global model efficiency considers the model outputs of the sub-group under study and all previous sub-groups in the calibration order. The calibrated parameter values are summarized in Table 3. Most of them are generally in agreement with literature values (among others, Jiang *et al.*, 2008; Fenu *et al.*, 2010; Hauduc *et al.*, 2011; Henze *et al.*, 2000). However, some values of the calibrated model parameters require further discussion. The calibrated value of μ_{AUT} (1.18 d^{-1}) is different from the value presented by Jiang (2007) who, applying the ASM2d-SMP model, obtained a value equal to 0.6 d^{-1}. The calibrated values of Y_H and b_H, respectively equal to 0.39 gX_H/gX_S and 0.58 d^1, correspond with values obtained independently by means of respirometric techniques (see Di Trapani *et al.*, 2011).

The calibrated value of q_{pp} (2.34 gX_{PP} gX_{PAO}^{-1} d^{-1}) is higher than the value obtained by Jiang (2007) (q_{pp} =1.1 gX_{PP} gX_{PAO}^{-1} d^{-1}). This parameter values takes into account the storage of poly-phosphate that in the analyzed plant was higher. Indeed, the orthophosphate assimilation took play not only in the aerobic tank but also in the anoxic one. Furthermore this parameter value takes into account the increasing of storage rate due to the K_2PO_4 dosing.

The model calibration results showed an acceptable correspondence with experimental data (final model efficiency equal to 0.36) demonstrating that the calibrated model was able to describe the behaviour of the pilot plant in an acceptable way. The satisfactory responses of the calibrated model demonstrate the ability of the adopted calibration procedure to be used also for very complex models, by taking into account the results of a global instead of a local sensitivity analysis.

In Figure 2, for example, a good prediction accuracy with respect to the long-term behaviour of some model outputs and related efficiencies ($E_{SPO,1}$, $E_{SNH4,2}$, $E_{MLSS,2}$ and $E_{CODTOT,5}$) are observed.

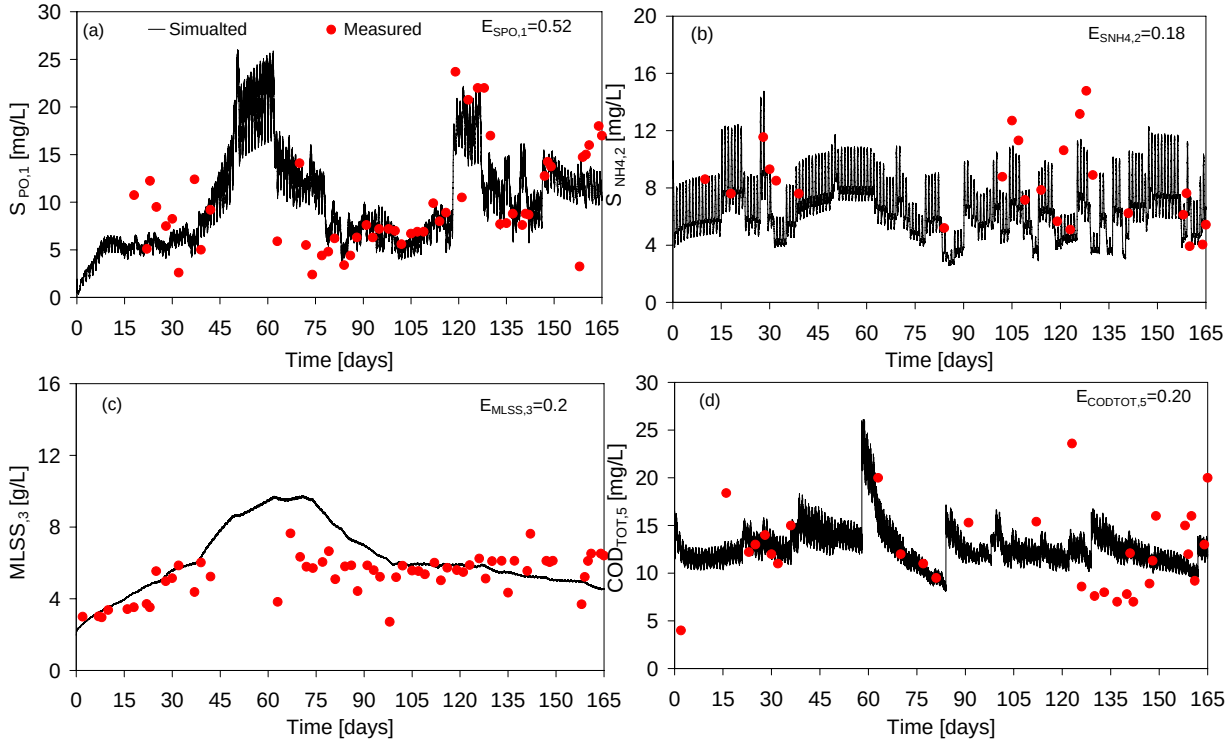


Figure 2 Simulated versus measured values for orthophosphate in the anaerobic tank ($S_{PO,1}$) (a), ammonia in the anoxic tank ($S_{NH4,2}$) (b), mixed liquor suspended solids in the aerobic tank ($MLSS_{,3}$) (c) and total COD in the permeate tank ($COD_{TOT,5}$) (d).

Important to note is that the model is able to reproduce the effect, in terms of $S_{PO,1}$ concentration (Figure 2(a)), of the influent KH_2PO_4 dosing (performed from day 117 to 127 in order to increase the influent P-PO_4 concentration). In terms of MLSS concentration (see Figure 2(c)) the model

over-predicts the simulated values from day 45 to day 90. Such results could be due to the model's incapacity to reproduce the stress condition of the biomass related to the frequent energy interruption in the pilot plant during this period. The same results which influence the mixed liquor COD_{TOT} have been found in all plant sections. As suggested by Lubello *et al*. (2009) such results could also be related to the fact that, especially in high sludge retention time (SRT) conditions, the fraction of particulates produced by the endogenous decay of biomass consists of new organic material. Regarding the $COD_{TOT,5}$ the good agreement between observed and simulated values is shown in Figure 2 (d), with the exception of the last period for which a modest mismatch is evident; the model is also able to reproduce the effect of the physical or chemical membrane cleaning (see the discontinuity around day 60 in Figure 2 (d)). In Figure 3 the simulated S_{UAP} and S_{BAP} profiles in the aerobic tank are shown**;** it is consistent with Jiang (2007) that an increase of SRT generates an increase in S_{UAP} until the beginning of sludge withdrawing.

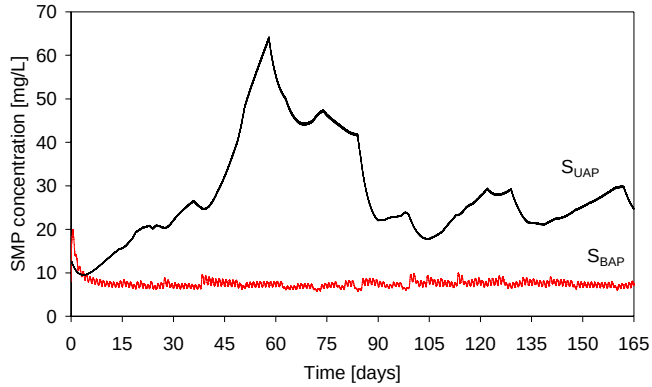


Figure 3 Simulated S_{UAP} and S_{BAP} profiles in the aerobic tank.

Globally, the best fit between simulated and measured data in terms of efficiency was obtained for $S_{PO,1}$ and $S_{PO,2}$ with efficiency values equal to 0.52 and 0.63 respectively. The global model efficiency after applying the calibration protocol was equal to 0.36 (computed as weighted sum among all 21 variables taken into account). This value has considerably increased compared to the value of 0.1 obtained by using the a priori values of the parameters obtained with the manual calibration. The results have undoubtedly been influenced by the data quality. Data collected during the sampling campaign were strongly influenced by unexpected events such as energy interruptions or non municipal discharges in the municipal sewer system of Palermo.

Conclusions

An integrated mathematical model able to describe the BNR processes and the cake layer contribution to the COD removal was presented. The model was calibrated by using an innovative calibration protocol by performing a preliminary sensitivity analysis to identify the most influential model parameters by means of the SRC method. By performing the global sensitivity analysis 24 influential model parameters were selected substantially reducing (>65%) the number of model parameters to calibrate and showing a good consistency between influential parameters and involved processes. Despite the model complexity the protocol provided acceptable results by applying a global sensitivity analysis, rarely used in the field of wastewater models, for the influential parameters screening. The simulated values of S_{UAP} and S_{BAP} were not used to calibrate the model due to a lack of measured values. However, the low modelled values of SMP concentration were consistent with the reversible membrane fouling noticed during the pilot plant operation. The integrated model represents a useful tool to improve MBR plant design and to pre-emptively evaluate the SMP concentration in an MBR system.

Acknowledgements

Peter Vanrolleghem holds the Canada Research Chair in Water Quality Modelling.

References

APHA, AWWA, WEF (1998). Standard Methods for the Examination of Water and Wastewater, 20th ed. American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA

Beven, K. J. and Binley, A. (1992). The future of distributed models: model calibration and uncertainty prediction. Hydrological Processes 6(3), 279–298.

Brun, R., Kühni, M., Siegrist, H., Guejer, W. and Reichert, P. (2002). Practical identifiability of ASM2d parameters-systematic selection and tuning of parameter subsets. Water Research, 36, 4113–4127.

Cosenza, A., Mannina, G., Neumann, M.B., Vanrolleghem, P.A. and Viviani G. (2011). Global sensitivity analysis in ASM applications: comparison of different methods. In proceeding of Watermatex 2011, 8th IWA Symposium on Systems Analysis and Integrated Assessment. San Sebastiàn, Spain, June 20-22, 2011.

Di Bella, G., Mannina, G. and Viviani, G., (2008). An integrated model for physical-biological wastewater organic removal in a submerged membrane bioreactor: Model development and parameter estimation. Journal of Membrane Science, 322(1), 1-12.

Di Trapani, D., Capodici, M., Cosenza, A., Di Bella, G., Mannina, G., Torregrossa, M. and Viviani, G. (2011). Evaluation of biomass activity and wastewater characterization in a UCT-MBR pilot plant by means of respirometric techniques. Desalination, 269, 190–197.

Fenu, A., Guglielmi, G., Jimenez, J., Spèrandio, M., Saroj, D., Lesjean, B., Brepols, C., Thoeye, C. and Nopens, I. (2010). Activated sludge model (ASM) based modelling of membrane bioreactor (MBR) processes: A critical review with special regard to MBR specificities. Water Research, 44 (15), 4272-94.

Hauduc, H., Gillot, S., Rieger, L., Ohtsuki, T., Shaw, A., Takács, I. and Winkler, S. (2009). Activated sludge modelling in practice - An international survey. Water Science and Technology, 60 (8), 1943-1951.

Hauduc, H., Rieger, L., Ohtsuki, T., Shaw, A., Takács, I., Winkler, S., Héduit, A., Vanrolleghem, P.A. and Gillot, S. (2011). Activated sludge modelling: Development and potential use of a practical applications database. Water Science and Technology (in press).

Henze, M., Gujer, W., Mino, T. and van Loosdrecht M.C.M. (2000). Activated sludge models ASM1, ASM2, ASM2d and ASM3. IWA Task Group on Mathematical Modelling for Design and Operation of Biological Wastewater treatment, IWA Publishing, London, UK.

Jang, N., Ren, X., Cho, J. and Kim I.S. (2006). Steady-state modelling of biofuling potentials with respect to the biological kinetics in the submerged membrane bioreactor. Journal of Membrane Science, 284, 352–360.

Jeppsson, U. (1996). Modelling aspect of wastewater treatment process. PhD thesis, Department of Industrial Electrical Engineering and Automation (IEA) Lund Institute of Technology (LTH), Sweden.

Jiang, T. (2007). Characterization and Modelling of Soluble Microbial Products in Membrane Bioreactors. PhD thesis, Ghent University, Belgium.

Jiang, T., Myngheer, S., De Pauw, D.J.W., Spanjers, H., Nopens, I., Kennedy, M. D., Amy, G. and Vanrolleghem, P.A., (2008). Modelling the production and degradation of soluble microbial products (SMP) in membrane bioreactors (MBR). Water Research, 42 (20), 4955–4964.

Jiang, T., Sin, G., Spanjers, H., Nopens, I., Kennedy, M., van der Meer, W., Futselaar, H., Amy G. and Vanrolleghem, P. A,, (2009). Comparison of the modeling approach between membrane bioreactor and conventional activated sludge processes. Water Environment Research, 81 (4), 432-440.

Innocenti, V. (2005). Modello di depurazione biologica secondo lo standard ASM3 con doppio step di nitrificazione. Degree Thesis. Università degli Studi di Firenze, Italy (in italian).

Kuberkar, V.T. and Davis, R.H. (2000). Modeling of fouling reduction by secondary membranes. Journal of Membrane Science, 168, 243–257.

Li, X. and Wang, X. (2006). Modelling of membrane fouling in a submerged membrane bioreactor. Journal of Membrane Science, 278, 151–161.

Lubello, C., Caffaz, S., Gori, R. and Munz, G. (2009). A modified Activated Sludge Model to estimate solids production at low and high solids retention time. Water Research, 43 (18), 4539–4548.

Mannina, G., Di Bella, G. and Viviani, G. (2010). Uncertainty assessment of a membrane bioreactor model using the GLUE methodology. Biochemical Engineering Journal, 52(2) 263–275.

Mannina, G., Cosenza, A., Vanrolleghem, P. A. and Viviani, G.. A practical protocol for calibration of nutrient removal wastewater treatment models. Journal of Hydroinformatics (in press).

Monclús, H., Sipma, J., Ferrero, G., Comas, J. and Rodriguez-Roda, I. (2010). Biological nutrient removal in an MBR treating municipal wastewater with special focus on biological phosphorus removal. Bioresource Technology, 101, 3984-3991.

Munz, G., De Angelis, D., Goria, R., Moric, G., Casarci, M. and Lubello, C. (2008). Process efficiency and microbial monitoring in MBR and conventional activated sludge process treatment of tannery wastewater. Bioresource Technology, 99 (18), 8559–8564.

Ng, H.Y.and Kim, A.S. (2007). A mini-review of modelling studies on membrane bioreactor (MBR) treatment for municipal wastewaters. Desalination 212, 261–281.

Rieger, L., Koch, G., Kühni, M., Gujer, W. and Siegrist, H. (2001). The EAWAG Bio-P module for activated sludge model No.3. Water Research 35(16), 3887–3903.

Saltelli, A., Tarantola, S., Campolongo, F. and Ratto, M. (2004). Sensitivity Analysis in Practice: A Guide to Assessing Scientific Models. John Wiley & Sons, Ltd.

Sin, G., Gernaey, Krist V., Neumann, M.B., van Loosdrecht, M.C.M. and W. Gujer (2011). Global sensitivity analysis in wastewater treatment plant model applications: Prioritizing sources of uncertainty. Water Research, 45, 639-651

Sperandio, M. and Espinosa, M.C. (2008). Modelling an aerobic submerged membrane bioreactor with ASM models on a large range of sludge retention time. Desalination, 231 (1-3), 82-90.

Yang, W.B., Cicek, N. and Ilg, J. (2006). State-of-the-art of membrane bioreactors: Worldwide research and commercial applications in North America. Journal of Membrane Science, 270 (1-2), 201-211.

Weijers, S. R. and Vanrolleghem, P. A. (1997). A procedure for selecting best identifiable parameters in calibrating activated sludge model No.1 to full-scale plant data. Water Science and Technology, 36(5), 69–79.

Zhang, H., Wang , X., Xiao, J., Yang, F. and Zhang, J. (2009). Enhanced biological nutrient removal using MUCT–MBR system. Bioresource Technology, 100, 1048–1054.