Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Modelling the production and degradation of soluble microbial products (SMP) in membrane bioreactors (MBR)

Tao Jiang[a,b,*], Silvie Myngheer[a], Dirk J.W. De Pauw[a], Henri Spanjers[a], Ingmar Nopens[a], Maria D. Kennedy[b], Gary Amy[b], Peter A. Vanrolleghem[a,c]

[a]BIOMATH, Department of Applied Mathematics, Biometrics and Process Control, Ghent University, Coupure Links 653, B-9000 Gent, Belgium
[b]UNESCO-IHE for Water Education, PO Box 3015, 2601 DA Delft, The Netherlands
[c]modelEAU, Département de génie civil, Pavillon Pouliot, Université Laval, Québec G1 K 7P4, Canada

ARTICLE INFO

Article history:
Received 26 March 2008
Received in revised form
2 July 2008
Accepted 16 September 2008
Published online 11 October 2008

Keywords:
Membrane bioreactor
Soluble microbial products
Activated sludge model
Membrane fouling

ABSTRACT

MBR biochemical conditions have an effect on membrane fouling and SMP have been attributed to be the main MBR foulant. Thus, predicting the SMP concentration is essential for understanding and controlling MBR fouling. However, existing SMP models are mostly too complex and over-parameterized, resulting in inadequate or absent parameter estimation and validation. This study extends the existing activated sludge model No. 2d (ASM2d) to ASM2dSMP with introduction of only 4 additional SMP-related parameters. Dynamic batch experimental results were used for SMP parameter estimation leading to reasonable parameter confidence intervals. Finally, the ASM2dSMP model was used to predict the impact of operational parameters on SMP concentration. It would found that solid retention time (SRT) is the key parameter controlling the SMP concentration. A lower SRT increased the utilization associated products (UAP) concentration, but decreased the biomass associated products (BAP) concentration and vice versa. A SRT resulting in minimum total SMP concentration can be predicted, and is found to be a relatively low value in the MBR. If MBRs operate under dynamic conditions and biological nutrient removal is required, a moderate SRT condition should be applied.

1. Introduction

Recent MBR studies treating municipal wastewater have reported a significant impact of biochemical process conditions on membrane fouling, e.g. DO (Dissolved Oxygen), SRT (Solid Retention Time), and HRT (Hydraulic Retention Time), etc. A short review is given below.

As a general trend, a high bioreactor DO leads to a better filterability and a lower fouling rate. This has been explained by either a lower specific cake resistance of the fouling layer (Kang et al., 2003; Kim et al., 2006) or a decreased amount of smaller flocs (Jin et al., 2006; Kim et al., 2006). Increasing the SRT leads to a better filterability in the range of SRTs of 2–10 days (Trussell et al., 2006), 8–80 days (Nuengjamnong et al., 2005) and 10–40 days (Liang et al., 2007). The higher fouling rate under lower SRT conditions is either attributed to the higher amount of SMP (soluble microbial products) (Liang et al., 2007) or the lower amount of bound EPS (Extracellular Polymeric Substances) (Nuengjamnong et al., 2005). However, further increasing SRT from 30 to 100 days has been reported to intensify fouling due to the accumulation of foulant and a higher sludge viscosity (Han et al., 2005). Decreasing HRT leads to a higher fouling rate for HRT of 4–10 h due to an increase in EPS concentrations (Chae et al., 2006). However, from the viewpoint of both membrane fouling control and economical design, the HRT should not be too high, and an optimal HRT of 12 h has been suggested (Tay et al., 2003).

* *Corresponding author*. Present address: ENVIRON China, Suite 14-E, New Hualian Mansion E. Building, No.755 Huaihai Road (M), Shanghai 200020, China. Tel.: +86 21 6473 6885; fax: +86 21 6473 6882.
E-mail address: tao.jiang@biomath.ugent.be (T. Jiang).
0043-1354/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.watres.2008.09.037

Nomenclature[1]

ASM	Activated Sludge Model
BAP	Biomass Associated Products
BSA	Bovine Serum Albumin
DO	Dissolved Oxygen
EPS	Extracellular Polymeric Substances
f_{BAP}	fraction of BAP produced during cell lysis
f_{UAP}	fraction of UAP produced during substrate uptake
HRT	Hydraulic Retention Time
K_{BAP}	half-saturation coefficient of BAP
$k_{h,BAP}$	hydrolysis rate of BAP
$k_{h,UAP}$	hydrolysis rate of UAP
LC-OCD	Liquid Chromatography-Organic Carbon Detection
MBR	Membrane Bioreactor
MLSS	Mixed Liquor Suspended Solids
MW	Molecular Weight
OUR	Oxygen Uptake Rate
PAO	Phosphorus Accumulating Organism
PHA	Polyhydroxyalkanoate
PHB	polyhydroxybutyrate
r_{SBAP}	production/consumption rate of BAP
S_0	substrate concentration
S_{BAP}	BAP (COD units)
SCOD	Soluble COD
SMP	Soluble Microbial Products
SRT	Solid Retention Time
S_{UAP}	UAP (COD units)
TCOD	Total COD
UAP	Utilization Associated Products
UAP_{COD}	UAP as COD unit
UAP_{pro}	UAP produced during cell proliferation phase
UAP_{PS}	polysaccharide content of UAP
UAP_{PT}	protein content of UAP
UAP_{sto}	UAP produced during substrate storage phase
VFA	Volatile Fatty Acids
X_0	MLSS concentration
X_H	heterotrophic biomass concentration
Y_{ASM2d}	yield of heterotrophs and PAO in ASM2d
$Y_{ASM2dSMP}$	yield of heterotrophs and PAO in ASM2dSMP
μ_{BAP}	biomass growth rate on BAP

A recurring problem in most literature is that rarely one operational parameter is varied at a time while all others are held constant, e.g. increasing SRT by reducing sludge wastage results in an increase in sludge concentration, viscosity, and oxygen demand but reduces biomass growth rate. Thus, fundamental studies are needed to identify the main foulant and the main influencing operational parameters.

SMP are typically divided into two categories: BAP (Biomass Associated Products), associated with biomass decay, and UAP (Utilization Associated Products), associated with substrate uptake and biomass growth (Rittmann et al., 1987). SMP are reported to build up to a high concentration in MBRs due to membrane retention (Huang et al., 2000; Shin and Kang, 2003). SMP have also been attributed to be the main MBR foulant (Rojas et al., 2005; Rosenberger et al., 2005, 2006).

The above review of MBR biochemical conditions, SMP, and membrane fouling raises the hypothesis that biochemical conditions, i.e. DO, SRT and HRT, affect MBR fouling indirectly through changes in SMP, EPS, and floc size, etc. Thus, predicting the SMP concentration using a mathematical model would be of primary interest in the study of MBR fouling. Mathematical modelling studies have already been conducted to predict the BAP and UAP concentrations in biological wastewater treatment processes. A critical review is given below.

Rittmann and coworkers have presented a series of SMP models. Their SMP studies were summarized and were presented as a unified SMP and EPS theory (Laspidou and Rittmann, 2002a, b). UAP and EPS are produced proportional to the substrate utilization rate and BAP are described as hydrolysis products of EPS. The same yield coefficients but different degradation rates (using a Monod kinetic structure) are assigned to UAP and BAP, respectively. This unified theory introduces 8 SMP-associated model parameters. However, most of these parameters were either given parameter values obtained in an early biofilm system (Namkung and Rittmann, 1986) or from literature.

Boero et al. (1991, 1996) have performed an SMP mass balance using a radio-active ^{14}C tracer. Three types of SMP are produced, i.e. soluble biodegradable (SMP_{SD}) and non-biodegradable (SMP_{ND}) (SMP_{SD} and SMP_{ND} are equivalent to UAP) and non-biodegradable SMP_E (equivalent to BAP). SMP_{SD} and SMP_{ND} are produced proportional to substrate uptake and SMP_E production is stoichiometrically related to biomass decay. SMP_{SD} can be degraded directly at a first-order rate with respect to SMP_{SD} and biomass concentration. Boero's model introduces only 3 stoichiometric and 1 kinetic SMP-associated parameters. The model is also calibrated using batch experimental results. However, the assumption that BAP are non-biodegradable lacks experimental evidence and model validation is not performed.

The SMP concept has been incorporated into activated sludge model No. 1 (ASM1) (Orhon et al., 1989; Artan et al., 1990). Firstly, a very simple SMP model including only BAP is developed (Orhon et al., 1989). So-called S_P (equivalent to BAP) is produced proportional to the hydrolysis of particulate COD (X_S) and they are assumed non-biodegradable. The model is further developed to include UAP (Artan et al., 1990). However, this model mixes the concepts and degradation kinetics of UAP and BAP resulting in strong parameter correlations. Moreover, the model lacks experimental support.

Lu and coworkers have incorporated a very complex SMP model into ASM1 (Lu et al., 2001) and ASM3 (Lu et al., 2002) in MBR studies. However, the COD of their SMP model is not balanced, i.e. the consumption of substrate is not equal to the sum of UAP, biomass and oxygen. In addition, 8 SMP-related parameters are introduced, but the experimental results available for model calibration are limited to steady state soluble COD (SCOD) measurements. Thus, the fitting is not convincing in demonstrating the validity of the model structure and parameter values. Ahn and co-authors have adapted similar SMP models to an MBR, but their model also suffers

[1] Note: The nomenclature for ASM2d parameters is not listed here. They can be found in Henze et al. (2000).

from a lack of appropriate calibration (Lee et al., 2002; Cho et al., 2003; Ahn et al., 2006).

The above review of existing SMP models exhibits very heterogeneous model structures. Some models only consider BAP production and assume BAP to be non-biodegradable. Others include the production and degradation of both BAP and UAP. A common problem of these models is that the models are too complex and over-parameterized. Indeed, the available measurements for model calibration are usually limited. Thus, the validity of the SMP model structure and the obtained parameter values are questionable.

ASM models (Henze et al., 2000) were developed due to the increased interest in biological nutrient removal in municipal wastewater treatment. ASM1 and 3 only describes COD and nitrogen removal. ASM2d is a further development of ASM2 and regarded as a powerful tool to describe COD, nitrogen and phosphorus removal. The ASM2d classifies biomass into three groups, i.e. ordinary heterotrophs (oxidise organics using oxygen or nitrate), nitrifiers (oxidise ammonium to nitrate), and phosphorus accumulating organisms (special heterotrophs with the ability to store phosphate in excess amount). The COD components in the ASM2d are classified as soluble and particulate. The soluble COD components are either inert (S_I) or biodegradable, i.e. acetate (S_A) and fermentable (S_F) COD. However, the ASM2d does not include SMP as COD component, although they are produced in the activated sludge process (Grady et al., 1972).

Given the interest in simultaneous study of MBR fouling and biological nutrient removal, it is valuable to extend the ASM2d model with SMP components. Thus, the objectives of this study are (1) to extend the ASM2d model with BAP and UAP components, and (2) to evaluate, through simulation, the impact of operational parameters on the SMP concentration. The simulated SMP concentration could be used in further model development in predicting MBR fouling. The added value of this study compared with the previous SMP studies are that (1) it focuses on minimising model complexity and parameter correlations, and (2) it uses dynamic data employing new analytical tools for model calibration.

2. Materials and methods

A lab-scale MBR was set up for COD and biological nutrient removal with a flow rate of 108 L/day. The reactor was fed with a sewage-like synthetic wastewater (composition adapted from Boeije et al., 1999) and operated under a total SRT of 17 days, an aerobic SRT of 7.2 days and an HRT of 6.4 h. The bioreactor was divided into an anaerobic and an aerobic/anoxic compartment. Alternating aeration (17 min DO = 1.5–2.5 mg/L, 23 min DO = 0) was applied in the aerobic/anoxic compartment for nitrification and denitrification. A tubular PVDF membrane (X-Flow, The Netherlands) with a nominal pore size of 0.03 μm (200 kDa) and a membrane surface area of 0.17 m^2 was used for biomass separation in a side-stream configuration. The membrane module was operated under air-lift mode at 31.8 L/(m^2 h) and both crossflow velocities for feed sludge and air were controlled at 0.5 m/s. A more detailed description of the MBR setup is provided by Jiang (2007).

Influent characteristics were measured twice per week. The effluent COD, NO_3^--N, and PO_4^{3-}-P were monitored daily. The effluent NH_4^+-N, NO_2^--N, TN, TP, COD and sludge total COD were monitored twice per week.

For batch experiments, fresh sludge was taken from the aerobic/anoxic compartment of the MBR, washed with dilution water (prepared by using Milli-Q water and having the same inorganic contents as the influent) and used to run three batch experiments. All experiments were conducted under conditions of constant temperature (15 °C) and controlled pH (7.5 ± 0.2). The BAP batch experiment was conducted under starvation conditions without substrate addition. Hence, the produced SMP should be dominated by BAP. Alternating aeration was applied to maintain the same aerobic:anoxic time ratio as in the lab-scale MBR: 49.4 min aerobic (on/off aeration, DO = 1.5–2.5 mg/L) and 70.6 min anoxic. The UAP batch experiment was spiked with acetate (end concentration of 1000 mg/L) under completely aerobic conditions (on/off aeration, DO = 1.5–2.5 mg/L). Meanwhile, a reference batch experiment was conducted without acetate addition to obtain the background SMP concentration. Thus, the net UAP concentration was calculated by subtracting the SCOD concentration in the reference experiment from that in the UAP experiment. This method eliminates the simultaneously produced BAP in the UAP batch.

The oxygen uptake rate (OUR) in the UAP batch was estimated by a linear fitting of the DO-time curve in the period when aeration was off. A Matlab program was developed to identify the linear section and calculate the slope (OUR). The biomass yield was estimated according to the integrated exogenous OUR and added acetate amount (Vanrolleghem et al., 1999).

SCOD was assessed using 0.45 μm filters (DURAPORE 0.45 μm PVDF, Millipore, USA). Proteins and polysaccharides were measured using colorimetric methods (Lowry et al., 1951; Dubois et al., 1956, respectively). LC-OCD (liquid chromatography-organic carbon detection) analysis was performed by a commercial lab DOC-LABOR (Dr. Huber, Germany, Huber and Frimmel, 1991). The liquid chromatography separates the organic components according to their molecular weight. Three detectors, i.e. UV absorbance at 254 nm, organic carbon and organic nitrogen, were connected in series to characterise the separated organic components online.

In the UAP batch, the external substrate acetate is also measured as SCOD. To eliminate the remaining acetate and obtain the net UAP, two approaches have been applied: (1) use LC-OCD to differentiate SMP from acetate; and (2) measure the protein and polysaccharide concentrations and estimate the UAP concentration using Eq. (1). The UAP_{COD}, UAP_{PT} and UAP_{PS} are the net UAP concentrations (concentrations obtained in the UAP batch minus those in the reference batch) as COD, proteins and polysaccharides, respectively. The constants 1.5 and 1.07 g COD/g substrate are conversion factors from polysaccharides and proteins to COD, respectively, by assuming that BSA (Bovine Serum Albumin) represents proteins and dextran represents polysaccharides. The constant 0.64 is a correction factor accounting for the underestimation of polysaccharides and proteins using the colorimetric methods (Rosenberger et al., 2005). In this study, this factor was estimated from 4-month average measurements of the MBR sludge water (filtrate of MBR sludge using 0.45 μm filter).

$$UAP_{COD} = (1.5UAP_{PT} + 1.07UAP_{PS})/0.64 \quad (1)$$

The modelling and simulation software WEST (MOSTforWATER NV, Kortrijk, Belgium) was used to perform model simulations and parameter estimations.

3. Results and discussion

3.1. ASM2d model calibration for the lab-scale MBR

The lab-scale MBR was first calibrated using the standard IWA ASM2d model (Henze et al., 2000). The key points of calibration are shortly described below. The details of calibration can be found in Jiang (2007).

The two bioreactors and the volume in the feed side of the membrane loop were treated as completely mixed reactors, which was justified based on the results of a tracer test. The membrane was assumed to retain all particulates (X_S, X_I and biomass), but allowed passing of all solutes (S_{NH}, S_{NO}, S_{PO}, S_F, S_A and S_I). The periodical membrane backwashing and relaxation was normalized as continuous flow. This simplified model was compared with a complete model describing the membrane backwashing and relaxation. The difference between the simulation results of these two approaches was found insignificant.

The influent wastewater was basically characterized using the STOWA protocol (Roeleveld and van Loosdrecht, 2002) with modification. The decay rate of the autotrophic biomass was obtained from batch experiments. The majority of the remaining parameters were taken as the defaults from the ASM2d. A few parameters (Table 1) were tuned during dynamic calibration to achieve a better fit of both in-cycle dynamic data (obtained from a measurement campaign) and 4-month average steady state measurements. The sequential methodology proposed by Hulsbeek et al. (2002) and extended by Insel et al. (2006) was used to calibrate the nitrification, denitrification, and biological phosphorus removal related parameters of the model.

Comparing the model predicted sludge and effluent concentration with measurements, the ASM2d model well predicted the mean sludge concentration and effluent quality.

Table 1 – Summary of calibrated ASM2d parameters (20 °C)

Parameter name	Symbol	Unit	Default	Calibrated
Decay rate of nitrifiers	b_{aut}	1/d	0.15	0.055
Maximum growth rate of nitrifiers	μ_{aut}	1/d	1	0.6
Oxygen half-saturation coefficient of nitrifiers	$K_{O,aut}$	mg O_2/L	0.5	0.2
Ammonium half-saturation coefficient of nitrifiers	$K_{NH_4,aut}$	mg N/L	1	0.2
Reduction factor of anoxic growth of heterotrophs	$\eta_{NO_3,het}$	–	0.8	1
Fermentation rate of acetate production	q_{fe}	1/d	3	1
PHA storage rate	q_{PHA}	1/d	3	5
Phosphate uptake rate	q_{pp}	1/d	1.5	1.1
Reduction factor of anaerobic hydrolysis	$\eta_{NO_3,PAO}$	–	0.6	0.4

However, it failed in predicting the SCOD of sludge water due to the overlook of SMP in the ASM2d (Table 3). The simulated SCOD in the sludge water (4.5 mg/L) only contained S_F, S_A and S_I. However, the actually measured SCOD (87.4 mg/L) also contained colloidal organics retained by the membrane. However, it should be noted that although it overlooks SMP, the ASM2d still allowed good prediction of COD and biological nutrient removal processes. If the objective of modelling is limited to this perspective, ASM2d is valid for MBR. Hence, the model extension proposed below is only of interest if SMP and MBR fouling are pursued.

3.2. ASM2dSMP model development and parameter estimation

The ASM2d model was extended to ASM2dSMP by introducing two new components: S_{BAP} and S_{UAP}. The general model assumptions are: (1) SMP are defined as colloids and solutes smaller than 0.45 μm and thus SMP can only be partially retained by MBR membranes; (2) both BAP and UAP are produced; and (3) both BAP and UAP are biodegradable with the same biomass yield coefficient (Y_H) but at a lower degradation rate than readily biodegradable substrate.

3.2.1. BAP production and degradation

The production of BAP can be described either as proportional to the biomass decay with a stoichiometric parameter (Boero et al., 1991, 1996) or with a separate rate constant (e.g. Laspidou and Rittmann, 2002a, 2002b; Lu et al., 2001, 2002). Both approaches are similar. Due to its simplicity, the former approach was adopted here by introducing a stoichiometric parameter f_{BAP} into the biomass lysis process in ASM2d. Thus, biomass lysis produces BAP in addition to inert particulate COD (X_I) and slowly biodegradable COD (X_S) as depicted in the Petersen matrix (Table 4).

Many earlier SMP studies assume that biomass can grow on BAP directly (Eq. (2)). However, 63% of the BAP have been shown to have a molecular weight (MW) larger than 20 kDa (Jiang, 2007), suggesting it would be highly unlikely that such large molecules can directly pass cell membranes. Degradation of large molecular organics typically occurs through a series of processes, e.g. adsorption, extracellular enzymatic hydrolysis of complex organic molecules to simpler ones, and uptake of the hydrolysed products (Dold et al., 1980). Thus, it is more likely that BAP are first hydrolysed, yielding fermentable COD (S_F) as defined in ASM2d. The BAP hydrolysis rate can be described either as a Monod type surface reaction, as in ASM2d (Eq. (3)), or as a simple first-order reaction with respect to BAP and biomass concentration (Eq. (4)).

Direct growth with Monod type kinetics :

$$r_{S_{BAP}} = \mu_{BAP}\frac{S_{BAP}}{K_{BAP}+S_{BAP}}X_H \quad (2)$$

Hydrolysis with Monod type surface reaction :

$$r_{S_{BAP}} = k_{h,BAP}\frac{S_{BAP}/X_H}{K_{BAP}+S_{BAP}/X_H}X_H \quad (3)$$

Hydrolysis with first order kinetics : $r_{S_{BAP}} = k_{h,BAP}S_{BAP}X_H$ (4)

All three forms of the BAP degradation process (Eqs. (2)–(4)), together with the BAP production process, were incorporated

Table 2 – Calibrated parameters of ASM2dSMP and comparison with the default ASM2d parameter values

Parameter	Description	Unit	ASM2d_calibrated		ASM2dSMP_calibrated		ASM2d_Default Value
			Value	Method	Value	Method	
b_{AUT}	Decay rate of autotroph	1/d	0.055	Batch test	0.055	Batch test	0.15
i_{N,X_S}	N content of X_S	gN/gCOD	0.035	Measure	0.035	Measure	0.04
i_{P,S_F}	P content of S_F	gP/gCOD	0	Measure	0	Measure	0.01
i_{P,X_S}	P content of X_S	gP/gCOD	0.005	Measure	0.005	Measure	0.01
$K_{NH,AUT}$	Saturation coefficient for ammonium (substrate)	mg N/L	0.2	Fit	0.2	Fit	1
$K_{O,AUT}$	Saturation coefficient for oxygen	mg O_2/L	0.2	Fit	0.2	Fit	0.5
μ_{AUT}	Maximum growth rate of autotroph	1/d	0.6	Fit	0.6	Fit	1
$\eta_{NO,Het}$	Reduction factor for denitrification	–	1	Fit	1	Fit	0.8
$\eta_{NO,PAO}$	Reduction factor for anoxic P uptake	–	0.4	Fit	0.6	Fit	0.6
q_{fe}	Maximum rate for fermentation	1/d	1	Fit	3	Fit	3
q_{PHA}	Rate constant for storage of X_{PHA}	1/d	5	Fit	6	Fit	3
q_{PP}	Rate constant for storage of X_{PP}	1/d	1.1	Fit	1.3	Fit	1.5
Y_H	Yield of heterotroph	mg COD/mg COD	0.625	Default	0.57	Mass balance	0.625
Y_{PAO}	Yield of PAO	mg COD/mg COD	0.625	Default	0.57	Mass balance	0.625
f_{BAP}	Fraction of BAP produced during cell lysis	–	n.a.		0.0215	Batch test	n.a.
$k_{h,BAP}$	Hydrolysis rate of BAP	1/d	n.a.		7.41×10^{-7}	Batch test	n.a.
f_{UAP}	Fraction of BAP produced during cell growth	–	n.a.		0.0963	Batch test	n.a.
$k_{h,UAP}$	Hydrolysis rate of UAP	1/d	n.a.		0.0102	Batch test	n.a.
$f_{nr,SMP}$	Percentage of non-retainable SMP	–	n.a.		0.081	Measure + fit	n.a.
$i_{N,SMP}$	N content of SMP	gN/gCOD	n.a.		0.07	Assume	n.a.
$i_{P,SMP}$	P content of SMP	gP/gCOD	n.a.		0.02	Assume	n.a.

Note: fit = fit the model to the results of measurement campaign and 4-month measurements.

into the ASM2d model for parameter estimation using a Simplex optimization algorithm. The BAP production and degradation processes using Monod type kinetics (Eqs. (2)–(3)) require estimating 3 parameters (f_{BAP}, μ_{BAP}, K_{BAP} in Eq. (2) or f_{BAP}, $k_{h,BAP}$, K_{BAP} in Eq. (3), respectively). In addition, the optimization algorithm tended to end its search in different local minima when different initial parameter estimates were chosen. This difficulty can be attributed to identifiability problems due to strong parameter correlation (Vanrolleghem et al., 1995). Conversely, the processes using first-order BAP hydrolysis kinetics (Eq. (4)) requires estimating only 2 parameters (f_{BAP} and $k_{h,BAP}$). All optimization runs using different initial parameter estimates converged to the same optimal parameter set (Fig. 1). Therefore, it was decided to describe the BAP degradation using the first-order kinetics.

Parameter confidence intervals were calculated from the parameter estimation error covariance matrix. A Hessian matrix was numerically estimated using the method of Nelder and Mead

Table 3 – Comparison of the ASM2dSMP model simulation with steady state experimental results

		4-month average	Standard deviation	Simulation (ASM2d)	Simulation (ASM2dSMP)
Waste sludge	Total COD (g COD/L)	10.90	0.65	10.83	10.85
Sludge water[a]	SCOD (mg COD/L)	87.4	22.7	4.5	92.5
(from waste sludge)	BAP (mg COD/L)	n.a.	n.a.	n.a.	77.5
	UAP (mg COD/L)	n.a.	n.a.	n.a.	10.5
Sludge water[a]	SCOD (mg COD/L)	107.4	33.4	5.0	107.5
(from membrane feed side)	BAP (mg COD/L)	n.a.	n.a.	n.a.	90.8
	UAP (mg COD/L)	n.a.	n.a.	n.a.	11.6
Effluent	COD (mg COD/L)	11.0	3.1	5.0	13.2
	BAP (mg COD/L)	n.a.	n.a.	n.a.	7.3
	UAP (mg COD/L)	n.a.	n.a.	n.a.	0.9
	TN (mg N/L)	10.2	2.8	8.8	9.6
	NH_4^+-N (mg N/L)	0.18	0.42	0.18	0.4
	NO_3^--N (mg N/L)	7.03	1.71	8.6	8.6
	NO_2^--N (mg N/L)	0.30	0.21	n.a.	n.a.
	PO_4^{3-}-P (mg P/L)	5.63	2.21	5.3	5.7

a Sludge water = sludge filtrate using 0.45 μm membrane filter.

Table 4 – Stoichiometry and kinetics of the BAP model (only new items to ASM2d are presented)

Processes	S_F	S_{BAP}	S_I	X_I	X_S	X_H	X_{PAO}	X_{AUT}	Rate
Aerobic Hydrolysis of BAP	$1-f_{SI}$	-1	f_{SI}						$k_{h,BAP}\frac{S_O}{K_O+S_O}S_{BAP}X_H$
Anoxic Hydrolysis of BAP	$1-f_{SI}$	-1	f_{SI}						$k_{h,BAP}\eta_{HNO_3}\frac{K_O}{K_O+S_O}\frac{S_{NO_3}}{K_{NO_3}+S_{NO_3}}S_{BAP}X_H$
Anaerobic Hydrolysis of BAP	$1-f_{SI}$	-1	f_{SI}						$k_{h,BAP}\eta_{fe}\frac{K_O}{K_O+S_O}\frac{K_{NO_3}}{K_{NO_3}+S_{NO_3}}S_{BAP}X_H$
Lysis of X_H		f_{BAP}		f_{xI}	$1-f_{xI}-f_{BAP}$	-1			$b_H X_H$
Lysis of X_{PAO}		f_{BAP}		f_{xI}	$1-f_{xI}-f_{BAP}$		-1		$b_{PAO}X_{PAO}\frac{S_{ALK}}{K_{ALK}+S_{ALK}}$
Lysis of X_{AUT}		f_{BAP}		f_{xI}	$1-f_{xI}-f_{BAP}$			-1	$b_{AUT}X_{AUT}$

(1965), resulting in a narrow 95% parameter confidence interval, i.e. $f_{BAP}=0.0215\pm0.0021$ and $k_{h,BAP}=(7.41\pm0.54)\times10^{-7}$ 1/d.

3.2.2. *UAP production and degradation*

The model description of the UAP production and degradation was also based on experimental observations. After the acetate addition, the net UAP production was estimated using Eq. (1) and is presented in Fig. 2. It should be noted that both UAP and BAP were produced after acetate addition. This method eliminated/reduced the interference of BAP and allowed a more accurate net UAP estimation and characterisation.

A more detailed UAP characterisation using LC-OCD was performed for samples collected at 2 h, 6.7 h and 23.3 h (Fig. 3). It appears that UAP were produced immediately after the acetate addition and degraded simultaneously. There was a net accumulation between 0 and 4 h, but most of the UAP was degraded subsequently between 4 and 8 h (Fig. 2). After around one day, high MW UAP (>20 kDa) accumulated (Fig. 3).

Following the measured net UAP concentration and LC-OCD characterisation, it is hypothesized that two types of UAP are produced in the cell growth phase. In phase 1 (storage, before 3.9 h), heterotrophic biomass takes up readily biodegradable substrate and stores it as, for instance, PHAs (polyhydroxyalkanoates). The UAP produced in this phase have a lower MW and are biodegradable. In phase 2 (proliferation, after 3.9 h), biomass utilizes the stored material and proliferation takes place (van Loosdrecht et al., 1997). The UAP produced in this phase have a higher MW and are probably more refractory (see the higher biopolymer peak of the net UAP after 23.3 h in Fig. 3).

Acetate used in this study is a well-known substrate that can easily be stored in the cell as PHB (polyhydroxybutyrate) (van Loosdrecht et al., 1997). The storage phenomenon in the UAP batch was confirmed by a very high apparent yield ($Y_H=0.83$) estimated from the OUR (oxygen update rate) data. Only UAP_{sto} were modelled and calibrated here. UAP_{pro} was not further studied due to the lack of experimental results after 8 h. All UAP in the model below refer to UAP_{sto} without specification.

Similar to the SMP models reviewed above, UAP production is assumed proportional to substrate utilization by introducing a stoichiometric parameter, f_{UAP}. Thus, substrate is utilized to produce UAP (f_{UAP}) in addition to growth (Y_H) and oxidation ($1-Y_H-f_{UAP}$) as depicted in Table 5.

Fig. 2 clearly demonstrates that UAP_{sto} were biodegradable and probably more readily biodegradable than BAP. Thus, a separate first-order kinetic parameter ($k_{h,UAP}$) was assigned to UAP hydrolysis (Eq. (5)). UAP parameters were estimated using a similar method as that of BAP resulting in $f_{UAP}=0.0963\pm0.0387$ and $k_{h,UAP}=0.0102\pm0.0044$ 1/d.

$$\text{First order UAP hydrolysis}: r_{S_{UAP}}=-k_{h,UAP}S_{UAP}X_H \quad (5)$$

However, the UAP model should be applied with caution: (1) the measured polysaccharides, proteins and equivalent UAP had quite high standard deviations (1.03, 0.63 and 5.34 mg/L,

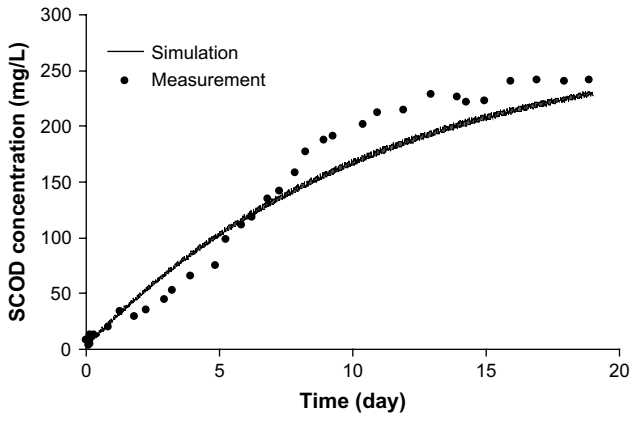

Fig. 1 – Simulated and measured SCOD concentration in a BAP batch experiment (SCOD is an estimate of the BAP concentration under starvation conditions).

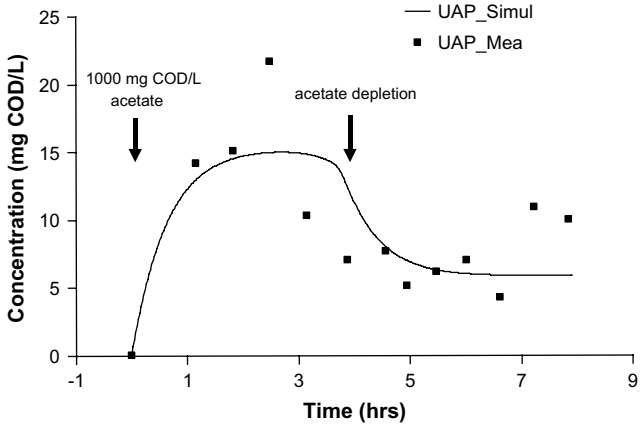

Fig. 2 – Simulated and measured net UAP concentration in the UAP batch experiment (1000 mg COD/L of acetate was added at 0 h).

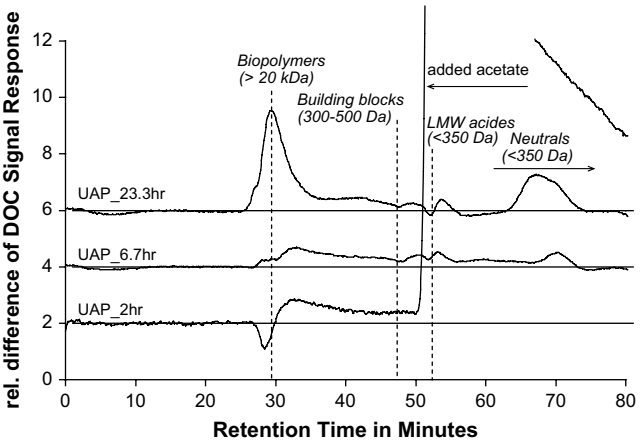

Fig. 3 – Differences of DOC signal between UAP and reference batches (net UAP production by subtracting the reference chromatogram from the UAP chromatogram) measured by LC-OCD.

respectively) due to their low concentrations; (2) only UAP_{sto} was included in the model and UAP_{pro} was not modelled; (3) a simple substrate, acetate, was used, whereas UAP production is known to be substrate specific (Boero et al., 1991, 1996); (4) a sewage-like synthetic wastewater was used as the MBR feed, whereas a real wastewater can produce different sludge and SMP characteristics; and (5) UAP production is related to the S_0/X_0 (substrate/MLSS) ratio at the start of the batch experiment. A low S_0/X_0 ratio (0.097) in a one-day batch test was used here, which is close to the common F/M ratio for nitrifying activated sludge processes. A higher S_0/X_0 ratio may produce a higher percentage of UAP due to more intensive cell proliferation (Hejzlar and Chudoba, 1986).

3.3. ASM2dSMP model validation for the lab-scale MBR

The ASM2dSMP model was validated using independent experimental results of a lab-scale MBR monitored under steady state conditions. The ASM2dSMP model parameters estimated in the SMP batch experiments (f_{BAP}, $k_{h,BAP}$, f_{UAP} and $k_{h,UAP}$) were directly used. Most ASM2d-related parameters were adapted directly from a calibrated ASM2d MBR model (Section 3.1). However, because of the model structure change, a few of them had to be adjusted as follows (Table 2).

First, the yield of X_H and X_{PAO} growth had to be adjusted according to the COD mass balance. In ASM2dSMP, a portion of the influent substrate COD is directed to UAP production, allowing additional X_H and X_{PAO} production from UAP. This can be easily compensated by decreasing their yields (Y_H and Y_{PAO}) from 0.625 to 0.57 using Eq. (6). The validity of this approach can be demonstrated by the fact that in this way the same simulated sludge concentrations are obtained in the ASM2d and ASM2dSMP (see Table 3).

$$Y_{ASM2d,SMP} = \frac{Y_{ASM2d}}{(1+f_{UAP})} \quad (6)$$

Second, the anaerobic acetate uptake rate and the aerobic/anoxic phosphorus uptake rate of PAO (Phosphorus Accumulation Organisms) were increased to fit the measured effluent phosphate concentration. In the previous ASM2d model calibration (Section 3.1), the default ASM2d parameters had to be adjusted to improve the anaerobic VFA (Volatile Fatty Acids) uptake and aerobic phosphorus uptake. However, the production of UAP in the ASM2dSMP model delayed the fermentation process (VFA production) and enabled restoration of some PAO-related parameters ($\eta_{NO,PAO}$ and q_{fe}) to their default ASM2d values.

Third, the percentage of non-retainable SMP ($f_{nr,SMP}$) should be estimated. The SCOD in the membrane feed side and effluent can be used to roughly estimate this key parameter. The first method estimating $f_{nr,SMP}$ yielded 0.059 by

Table 5 – Stoichiometry and kinetics of the UAP model (only new items to ASM2d are presented)

Processes	S_O	S_F	S_A	S_{UAP}	S_{NO}	S_I	X_H	X_{PAO}	X_{AUT}	Rate
Aerobic Hydrolysis of UAP		$1-f_{SI}$		-1		f_{SI}				$k_{h,UAP}\frac{S_O}{K_O+S_O}S_{UAP}X_H$
Anoxic Hydrolysis of UAP		$1-f_{SI}$		-1		f_{SI}				$k_{h,UAP}\eta_{HNO_3}\frac{K_O}{K_O+S_O}\frac{S_{NO_3}}{K_{NO_3}+S_{NO_3}}S_{UAP}X_H$
Anaerobic Hydrolysis of UAP		$1-f_{SI}$		-1		f_{SI}				$k_{h,UAP}\eta_{fe}\frac{K_O}{K_O+S_O}\frac{K_{NO_3}}{K_{NO_3}+S_{NO_3}}S_{UAP}X_H$
Aerobic growth of X_H on S_F	$-\frac{1-Y_H-f_{UAP}}{Y_H}$	$-\frac{1}{Y_H}$		$\frac{f_{UAP}}{Y_H}$			1			$\mu_H\frac{S_O}{K_O+S_O}\frac{S_F}{K_F+S_F}\frac{S_F}{S_A+S_F}\frac{S_{NH}}{K_{NH}+S_{NH}}\frac{S_{PO}}{K_{PO}+S_{PO}}\frac{S_{ALK}}{K_{ALK}+S_{ALK}}X_H$
Aerobic growth of X_H on S_A	$-\frac{1-Y_H-f_{UAP}}{Y_H}$		$-\frac{1}{Y_H}$	$\frac{f_{UAP}}{Y_H}$			1			$\mu_H\frac{S_O}{K_O+S_O}\frac{S_A}{K_A+S_A}\frac{S_A}{S_F+S_A}\frac{S_{NH}}{K_{NH}+S_{NH}}\frac{S_{PO}}{K_{PO}+S_{PO}}\frac{S_{ALK}}{K_{ALK}+S_{ALK}}X_H$
Anoxic growth of X_H on S_F		$-\frac{1}{Y_H}$		$\frac{f_{UAP}}{Y_H}$	$-\frac{1-Y_H-f_{UAP}}{2.86Y_H}$		1			$\mu_H\eta_{NO_3}\frac{K_O}{K_O+S_O}\frac{S_{NO_3}}{K_{NO_3}+S_{NO_3}}\frac{S_F}{K_F+S_F}\frac{S_F}{S_F+S_A}\frac{S_{NH_4}}{K_{NH_4}+S_{NH_4}}\frac{S_{PO_4}}{K_{PO_4}+S_{PO_4}}\frac{S_{ALK}}{K_{ALK}+S_{ALK}}X_H$
Anoxic growth of X_H on S_A			$-\frac{1}{Y_H}$	$\frac{f_{UAP}}{Y_H}$	$-\frac{1-Y_H-f_{UAP}}{2.86Y_H}$		1			$\mu_H\eta_{NO_3}\frac{K_O}{K_O+S_O}\frac{S_{NO_3}}{K_{NO_3}+S_{NO_3}}\frac{S_A}{K_A+S_A}\frac{S_A}{S_F+S_A}\frac{S_{NH_4}}{K_{NH_4}+S_{NH_4}}\frac{S_{PO_4}}{K_{PO_4}+S_{PO_4}}\frac{S_{ALK}}{K_{ALK}+S_{ALK}}X_H$
Aerobic growth of X_{PAO}	$-\frac{1-Y_H-f_{UAP}}{Y_H}$			$\frac{f_{UAP}}{Y_H}$				1		$\mu_{PAO}\frac{S_O}{K_O+S_O}\frac{S_{PO}}{K_P+S_{PO}}\frac{S_{NH}}{K_{NH}+S_{NH}}\frac{S_{ALK}}{K_{ALK}+S_{ALK}}\frac{X_{PHA}/X_{PAO}}{K_{PHA}+X_{PHA}/X_{PAO}}X_{PAO}$
Anoxic growth of X_{PAO} on NO_3^+				$\frac{f_{UAP}}{Y_H}$	$-\frac{1-Y_H-f_{UAP}}{2.86Y_H}$			1		$\eta_{NO_3}\mu_{PAO}\frac{K_O}{K_O+S_O}\frac{S_{NO_3}}{K_{NO_3}+S_{NO_3}}\frac{S_{PO}}{K_P+S_{PO}}\frac{S_{NH}}{K_{NH}+S_{NH}}\frac{S_{ALK}}{K_{ALK}+S_{ALK}}\frac{X_{PHA}/X_{PAO}}{K_{PHA}+X_{PHA}/X_{PAO}}X_{PAO}$
Growth of X_{AUT}	$-\frac{4.57-Y_A-f_{UAP}}{Y_A}$			$\frac{f_{UAP}}{Y_H}$	$\frac{1}{Y_A}$				1	$\mu_{AUT}\frac{S_O}{K_{OAUT}+S_O}\frac{S_{NH}}{K_{NHAUT}+S_{NH}}\frac{S_{PO}}{K_{PO}+S_{PO}}\frac{S_{ALK}}{K_{ALK}+S_{ALK}}X_{AUT}$

subtracting the S_I, S_F, and S_A (predicted by the ASM2d model) from the overall SCOD. It should be noted that errors exist in predicting the S_I, S_F, and S_A concentration, and hence the errors can be transferred to estimating $f_{nr,SMP}$. It is more reliable to estimate this key parameter by fitting the predicted SCOD in the membrane feed side to actual measurements. Thus, the second approach was adopted, which yielded $f_{nr,SMP} = 0.081$.

The comparison of ASM2dSMP and ASM2d model predictions with steady state experimental results is presented in Table 3. The simulated sludge and effluent concentrations using the ASM2dSMP showed very good agreement with the measurements. In addition, they are generally better than the simulation results using the ASM2d. Remarkably, the simulated SCOD of sludge water (92.5 mg/L) using ASM2dSMP was very close to the measurement (87.4 mg/L), whereas ASM2d predicted only 4.5 mg/L. The remarkable difference is due to the fact that the main constituent of MBR sludge water was actually SMP, which were modelled in the ASM2dSMP and described as partially retainable by the membrane.

3.4. *Comparison of the SMP model with literature*

Most SMP models reviewed above are complex and over-parameterized with strong parameter correlations. Moreover, few measurements (and mostly only steady state SCOD data) are available for parameter estimation. On top of that, model parameters are often estimated using trial and error methods, no parameter confidence interval is given and no independent model validations are conducted.

Contrary, in this study the SMP model structure development was based on experimental observations. A new analytical tool (LC-OCD) allowed a better SMP characterisation. To describe the SMP production and degradation, a simple model including only 4 SMP-related parameters was introduced and integrated with the ASM2d. Dynamic batch data were collected for BAP and UAP separately and used for parameter estimation, allowing more trust in parameter estimation and resulting in reasonable parameter confidence intervals. Finally, the developed SMP model was validated using independent MBR steady state measurements.

3.5. *Impact of MBR operational conditions on SMP*

As an application of ASM2dSMP, the impact of MBR operational conditions (such as SRT and HRT) on the expected SMP concentration was demonstrated by two series of model simulations for the lab-scale MBR. The first series of simulations varied the amount of sludge wastage (for a fixed HRT, leading to a varying SRT and SRT/HRT ratio). In the second series of simulations the reactor volume was varied (for a fixed SRT/HRT ratio, leading to a varying SRT and HRT). Each simulation was run for 500 days to reach steady state.

In both series of simulations, the predicted SMP concentration increased with the SRT (Fig. 4). However, the other operational parameters/variables, e.g. HRT, SRT/HRT and MLSS showed opposite trend with SMP under certain operational conditions. Hence, other operational parameters/variables do not directly control the SMP concentrations, but they can interact each other to impose indirect impacts. In conclusion, SRT is the key operational parameter controlling SMP concentration and eventually influences MBR fouling.

The simulations also demonstrate the impact of SRT on the BAP and UAP ratio. The UAP concentration decreased as SRT increased, but levelled off at an SRT above 15 days. Conversely, the BAP concentration always increased as SRT increased. Thus, there exists an ''optimal'' SRT resulting in a minimum total SMP (BAP + UAP) concentration. This optimum was found at an SRT of around 2 days for this lab-scale MBR.

Model demonstration of the existence of an optimal SRT minimising SMP is consistent with the UAP and BAP definition and early SMP experimental studies. Rittmann et al. (1987) reported an optimal SRT of 2 days using model simulation, while Pribyl et al. (1997) reported an optimal SRT of 5–15 days using experimental data.

However, the model predicted optimal SRT in this lab-scale MBR was lower than the 4 studies reviewed in Section 1. The difference can be attributed to very difference influent characteristics (synthetic and real wastewater) and operational conditions. The first 3 reviewed studies report that high SRT reduces MBR fouling in the range of lower SRT and lower MLSS conditions, i.e. 2–80 days and 3.07–7.82 g/L, respectively (Nuengjamnong et al., 2005; Trussell et al., 2006; Liang et al., 2007). The lower SRT and MLSS conditions imply that the biomass decay and BAP production are not significant. Whereas, the last study reports that high SRT intensifies MBR fouling in the range of higher SRT and higher MLSS conditions, i.e. 30–100 days and 7–18 g/L, respectively (Han et al., 2005). Thus, significant amount of BAP are produced and accumulate in the bioreactor, which therefore intensifies membrane fouling. This lab-scale MBR operated under moderate SRT (17 days) but higher MLSS conditions (10.9 g/L). The BAP production was therefore more significant than the UAP. Hence, the optimal SRT predicted by the model was lower. In addition, two of the reviewed studies showed that higher organic concentrations of sludge water intensify MBR fouling (Trussell et al., 2006; Liang et al., 2007). This is another support of SMP's impact on MBR fouling and the significance of predicting SMP concentrations in MBRs.

Care should be taken in applying the ASM2dSMP model and finding the optimal MBR operational conditions. Two model limitations have to be addressed as follows. (1) The conducted simulations only focused on the SMP concentrations under steady state. Dynamically varying process conditions have been reported to stimulate SMP production and to result in intensified membrane fouling (Evenblij et al., 2005; Drews et al., 2006). (2) The fouling potential of UAP and BAP may be different and the UAP may have a higher fouling potential than BAP (Jiang, 2007). Whereas, in the proposed SRT optimization, UAP and BAP were assumed to have equal fouling potential. Both of the above model limitations suggest that full-scale MBRs should operate under a higher SRT than the model prediction.

In addition to predicting the SMP concentration, the ASM2dSMP model maintains ASM2d's ability to simulate biological nutrient removal (BNR). For example, simulations showed the effluent ammonium concentration would be over 5 mg/L, if the MBR operated below an SRT of 13 days (data not shown). Typical BNR activated sludge processes operate under moderate SRT conditions. Therefore, if both BNR and

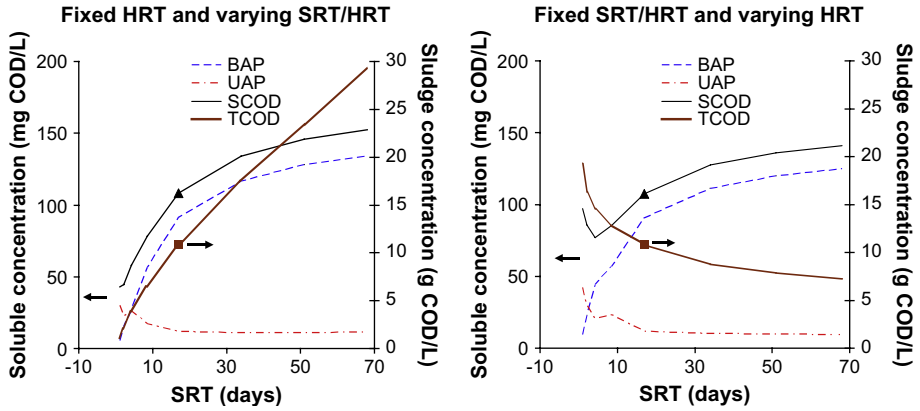

Fig. 4 – The impact of SRT on SMP and sludge concentration (lines = simulation results, ▲ = measured SCOD, ■ = measured TCOD).

membrane fouling control are set as objectives, a moderate SRT should be applied. The actual optimal SRT value needs further study, and will be related to the influent characteristics, the BAP and UAP characteristics, and the membrane characteristics under dynamic operational conditions.

4. Conclusions

Dedicated batch experiments were designed to produce BAP and UAP separately. Analyses using a new tool, LC-OCD, revealed that BAP and UAP were mostly composed of large molecular weight compound. Thus, unlike previous studies, the degradation of BAP and UAP was described to undergo a hydrolysis process producing fermentable soluble COD (S_F).

The ASM2d model was extended to ASM2dSMP, introducing only four additional parameters. Care was taken in minimising model complexity and parameter correlations, and as a consequence model parameter estimation resulted in reasonable confidence intervals. Finally, the ASM2dSMP model was successfully validated using independent experimental results of a lab-scale MBR under steady state conditions.

Finally, the ASM2dSMP model was used to predict the impact of operational parameters on SMP concentration. Model simulation showed that SRT is the key operational parameter controlling the predicted SMP concentration and eventually influencing MBR fouling. A lower SRT increased the UAP concentration, but decreased the BAP concentration and vice versa. An SRT resulting in minimum total SMP concentration could be predicted, and was found to be as low as 2 days in the MBR. Finally, if MBRs operate under dynamic conditions and biological nutrient removal is required, a moderate SRT should be applied.

Acknowledgments

This study was financially supported by Vitens Fryslân, The Netherlands. In addition, the authors wish to thank Norit/X-Flow for technical support and membranes. Lastly, we would like to thank Dr. Huber (DOC-LABOR) for his help in interpreting the LC-OCD analyses and Griet Schelstraete and Tinne De Boeck for performing the analytical work. Peter Vanrolleghem holds the Canada Research Chair on Water Quality Modelling. Ingmar Nopens is a postdoctoral fellow supported by the Ghent University Research Fund.

REFERENCES

Ahn, Y.T., Choi, Y.K., Jeong, H.S., Chae, S.R., Shin, H.S., 2006. Modeling of extracellular polymeric substances and soluble microbial products production in a submerged membrane bioreactor at various SRTs. Water Sci. Technol. 53 (7), 209–216.

Artan, N., Orhon, D., Baykal, B.B., 1990. Implications of the task group model. 1. The effect of initial substrate concentration. Water Res. 24 (10), 1251–1258.

Boeije, G., Corstanje, R., Rottiers, A., Schowanek, D., 1999. Adaptation of the CAS test system and synthetic sewage for biological nutrient removal – part I: development of a new synthetic sewage. Chemosphere 38 (4), 699–709.

Boero, V.J., Eckenfelder, W.W., Bowers, A.R., 1991. Soluble microbial product formation in biological-systems. Water Sci. Technol. 23 (4–6), 1067–1076.

Boero, V.J., Bowers, A.R., Eckenfelder, W.W., 1996. Molecular weight distribution of soluble microbial products in biological systems. Water Sci. Technol. 34 (5–6), 241–248.

Chae, S.R., Ahn, Y.T., Kang, S.T., Shin, H.S., 2006. Mitigated membrane fouling in a vertical submerged membrane bioreactor (VSMBR). J. Memb. Sci. 280 (1–2), 572–581.

Cho, J., Ahn, K.H., Seo, Y., Lee, Y., 2003. Modification of ASM no.1 for a submerged membrane bioreactor system: including the effects of soluble microbial products on membrane fouling. Water Sci. Technol. 47 (12), 177–181.

Dold, P.L., Ekama, G.A., Marais, G.R., 1980. A general-model for the activated-sludge process. Prog. Water Technol. 12 (6), 47–77.

Drews, A., Vocks, M., Iversen, V., Lesjean, B., Kraume, M., 2006. Influence of unsteady membrane bioreactor operation on EPS formation and filtration resistance. Desalination 192 (1–3), 1–9.

Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A., Smith, F., 1956. Colorimetric method for determination of sugars and related substances. Anal. Chem. 28 (3), 350–356.

Evenblij, H., Verrecht, B., van der Graaf, J.H.J.M., Van der Bruggen, B., 2005. Manipulating filterability of MBR activated

sludge by pulsed substrate addition. Desalination 178 (1–3), 193–201.
Grady, C.P.L., Harlow, L.J., Riesing, R.R., 1972. Effects of growth-rate and influent substrate concentration on effluent quality from chemostats containing bacteria in pure and mixed culture. Biotechnol. Bioeng. 14 (3), 391–410.
Han, S.S., Bae, T.H., Jang, G.G., Tak, T.M., 2005. Influence of sludge retention time on membrane fouling and bioactivities in membrane bioreactor system. Process Biochem. 40 (7), 2393–2400.
Hejzlar, J., Chudoba, J., 1986. Microbial polymers in the aquatic environment .1. Production by activated-sludge microorganisms under different conditions. Water Res. 20 (10), 1209–1216.
Henze, M., Gujer, W., Mino, T., van Loosdrecht, M., 2000. Activated Sludge Models: ASM1, ASM2, ASM2d and ASM3, Scientific And Technical Reports No. 9. IWA Publishing, London.
Huang, X., Liu, R., Qian, Y., 2000. Behaviour of soluble of microbial products in a membrane bioreactor. Process BioChem. 36 (5), 401–406.
Huber, S.A., Frimmel, F.H., 1991. Flow-injection analysis of organic and inorganic carbon in the low-ppb range. Anal. Chem. 63 (19), 2122–2130.
Hulsbeek, J.J.W., Kruit, J., Roeleveld, P.J., van Loosdrecht, M.C.M., 2002. A practical protocol for dynamic modelling of activated sludge systems. Water Sci. Technol. 45 (6), 127–136.
Insel, G., Sin, G., Lee, D.S., Nopens, I., Vanrolleghem, P.A., 2006. A calibration methodology and model-based systems analysis for SBRs removing nutrients under limited aeration conditions. J. Chem. Technol. Biotechnol. 81 (4), 679–687.
Jiang, T., 2007. Characterization and Modelling of Soluble Microbial Products in Membrane Bioreactors. Ph.D. thesis, Ghent University, Gent, Belgium.
Jin, Y.L., Lee, W.N., Lee, C.H., Chang, I.S., Huang, X., Swaminathan, T., 2006. Effect of DO concentration on biofilm structure and membrane filterability in submerged membrane bioreactor. Water Res. 40 (15), 2829–2836.
Kang, I.J., Lee, C.H., Kim, K.J., 2003. Characteristics of microfiltration membranes in a membrane coupled sequencing batch reactor system. Water Res. 37 (5), 1192–1197.
Kim, H.Y., Yeon, K.M., Lee, C.H., Lee, S., Swaminathan, T., 2006. Biofilm structure and extracellular polymeric substances in low and high dissolved oxygen membrane bioreactors. Sep. Sci. Technol. 41 (7), 1213–1230.
Laspidou, C.S., Rittmann, B.E., 2002a. Non-steady state modeling of extracellular polymeric substances, soluble microbial products, and active and inert biomasss. Water Res. 36 (8), 1983–1992.
Laspidou, C.S., Rittmann, B.E., 2002b. A unified theory for extracellular polymeric substances, soluble microbial products, and active and inert biomass. Water Res. 36 (11), 2711–2720.
Lee, Y., Cho, J., Seo, Y., Lee, J.W., Ahn, K.H., 2002. Modeling of submerged membrane bioreactor process for wastewater treatment. Desalination 146 (1–3), 451–457.
Liang, S., Cui, L., Song, L.F., 2007. Soluble microbial products in membrane bioreactor operation: behaviors, characteristics, and fouling potential. Water Res. 41, 95–101.
Lowry, O.H., Rosebrough, N.J., Farr, A.L., Randall, R.J., 1951. Protein measurement with the Folin phenol reagent. J. Biol. Chem. 193, 265–275.
Lu, S.G., Imai, T., Ukita, M., Sekine, M., Higuchi, T., Fukagawa, M., 2001. A model for membrane bioreactor process based on the concept of formation and degradation of soluble microbial products. Water Res. 35 (8), 2038–2048.
Lu, S.G., Imai, T., Ukita, M., Sekine, M., Higuchi, T., 2002. Modeling prediction of membrane bioreactor process with the concept of soluble microbial product. Water Sci. Technol. 46 (11–12), 63–69.
van Loosdrecht, M.C.M., Pot, M.A., Heijnen, J.J., 1997. Importance of bacterial storage polymers in bioprocesses. Water Sci. Technol. 35 (1), 41–47.
Namkung, E., Rittmann, B.E., 1986. Soluble microbial products (SMP) formation kinetics by biofilms. Water Res. 20 (6), 795–806.
Nelder, J.A., Mead, R., 1965. A simplex method for function minimization. Comput. J. 7, 308–313.
Nuengjamnong, C., Kweon, J.H., Cho, J., Polprasert, C., Ahn, K.H., 2005. Membrane fouling caused by extracellular polymeric substances during microfiltration processes. Desalination 179 (1–3), 117–124.
Orhon, D., Artan, N., Cimsit, Y., 1989. The concept of soluble residual product formation in the modeling of activated-sludge. Water Sci. Technol. 21 (4–5), 339–350.
Pribyl, M., Tucek, F., Wilderer, P.A., Wanner, J., 1997. Amount and nature of soluble refractory organics produced by activated sludge microorganisms in sequencing batch and continuous flow reactors. Water Sci. Technol. 35 (1), 27–34.
Rittmann, B.E., Bae, W., Namkung, E., Lu, C.J., 1987. A critical-evaluation of microbial product formation in biological processes. Water Sci. Technol. 19 (3–4), 517–528.
Roeleveld, P.J., van Loosdrecht, M.C.M., 2002. Experience with guidelines for wastewater characterisation in The Netherlands. Water Sci. Technol. 45 (6), 77–87.
Rojas, M.E.H., Van Kaam, R., Schetrite, S., Albasi, C., 2005. Role and variations of supernatant compounds in submerged membrane bioreactor fouling. Desalination 179 (1–3), 95–107.
Rosenberger, S., Evenblij, H., te Poele, S.T., Wintgens, T., Laabs, C., 2005. The importance of liquid phase analyses to understand fouling in membrane assisted activated sludge processes – six case studies of different European research groups. J. Memb. Sci. 263 (1–2), 113–126.
Rosenberger, S., Laabs, C., Lesjean, B., Gnirss, R., Amy, G., Jekel, M., Schrotter, J.C., 2006. Impact of colloidal and soluble organic material on membrane performance in membrane bioreactors for municipal wastewater treatment. Water Res. 40 (4), 710–720.
Shin, H.S., kang, S.T., 2003. Characteristics and fates of soluble microbial products in a ceramic membrane bioreactor at various sludge retention times. Water Res. 37 (1), 121–127.
Tay, J.H., Zeng, J.L., Sun, D.D., 2003. Effects of hydraulic retention time on system performance of a submerged membrane bioreactor. Sep. Sci. Technol. 38 (4), 851–868.
Trussell, R.S., Merlo, R.P., Hermanowicz, S.W., Jenkins, D., 2006. The effect of organic loading on process performance and membrane fouling in a submerged membrane bioreactor treating municipal wastewater. Water Res. 40 (14), 2675–2683.
Vanrolleghem, P.A., Vandaele, M., Dochain, D., 1995. Practical Identifiability of a biokinetic model of activated-sludge respiration. Water Res. 29 (11), 2561–2570.
Vanrolleghem, P.A., Spanjers, H., Petersen, B., Ginestet, P., Takacs, I., 1999. Estimating (combinations of) activated sludge model no. 1 parameters and components by respirometry. Water Sci. Technol. 39 (1), 195–214.