Comparison of the Modeling Approach between Membrane Bioreactor and Conventional Activated Sludge Processes

Tao Jiang^{1,*}, Gürkan Sin^{1,2}, Henri Spanjers¹, Ingmar Nopens¹, Maria D. Kennedy³, Walter van der Meer⁴, Harry Futselaar⁵, Gary Amy³, Peter A. Vanrolleghem^{1,6}

ABSTRACT: Activated sludge models (ASM) have been developed and largely applied in conventional activated sludge (CAS) systems. The applicability of ASM to model membrane bioreactors (MBR) and the differences in modeling approaches have not been studied in detail. A laboratory-scale MBR was modeled using ASM2d. It was found that the ASM2d model structure can still be used for MBR modeling. There are significant differences related to ASM modeling. First, a lower maximum specific growth rate for MBR nitrifiers was estimated. Independent experiments demonstrated that this might be attributed to the inhibition effect of soluble microbial products (SMP) at elevated concentration. Second, a greater biomass affinity to oxygen and ammonium was found, which was probably related to smaller MBR sludge flocs. Finally, the membrane throughput during membrane backwashing/relaxation can be normalized and the membrane can be modeled as a continuous flow-through point separator. This simplicity has only a minor effect on ASM simulation results; however, it significantly improved simulation speed. Water Environ. Res., 81, 432 (2009).

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Introduction

Membrane bioreactor (MBR) technology is a new development in the conventional activated sludge (CAS) process. The introduction of membrane filtration to replace a secondary clarifier overcomes several limitations in the CAS process such as settling problems from filamentous bulking, foaming, rising sludge, pinpoint sludge, and low mixed-liquor suspended solid (MLSS) concentration in the bioreactor (Casey et al., 1995; Jenkins et al., 2004). It also requires a smaller footprint than CAS.

The use of a membrane and a higher MLSS concentration creates differences compared to traditional CAS. First, MBR has a lower oxygen transfer efficiency because of the higher MLSS concentration (Cornel et al., 2003; Günder, 2001; Germain et al., 2007; Krampe and Krauth, 2003). In aeration systems, a correction factor (α) is defined as the ratio of the oxygen transfer coefficient (K_La) obtained in the activated sludge mixed liquor and the one obtained in clean water. The α decreases as a function of MLSS concentration. For example, Krampe and Krauth (2003) use a power law $[\alpha = \exp(-0.08788 \times X_{TSS})]$ to estimate the decrease in α factor of MBR sludge as the MLSS concentration increases from 1 to 28 g/L. Second, the sludge concentration in the front of the MBR (often an anaerobic zone) typically is much lower than that in the rear of the bioreactor (often the aerobic zone), where a membrane module is submerged (submerged configuration), or connected (side-stream configuration). However, the CAS system often returns concentrated secondary clarifier underflow to the front of the bioreactor. As a result, the sludge mass in MBRs is no longer proportional to the bioreactor volume as in CAS systems. The advantage is that the sludge mass distribution in MBRs can be manipulated flexibly by adjusting the internal recirculation flow rate (Ramphao et al., 2005).

Complete sludge retention in MBRs may change selection pressure on the biomass population from sludge settling properties (in CAS) to growth kinetics (in MBR) (Parco et al., 2006). Biomass with a higher substrate affinity and lower growth rate may obtain a competitive advantage over those with a lower substrate affinity and higher growth rate. However, this hypothesis still needs more experimental confirmation.

Unfortunately, studies comparing MBR and CAS under the same feed wastewater and operational conditions are rare. Gao et al. (2004) have reported that a submerged MBR develops significantly more nitrifiers than a reference CAS system, and its nitrification performance is more effective and stable. Conversely, Manser et al. (2005b) have reported that the community composition of ammonia-oxidizing bacteria and nitrite-oxidizing bacteria exhibits only a minor difference as indicated by fluorescent in situ hybridization results. Both systems exhibit the same maximum specific nitrification rates.

Some kinetic parameters of MBR sludge have been compared with those of CAS systems. Manser et al. (2005a) have studied the substrate and oxygen affinity of nitrifiers. They found that the halfsaturation coefficients for the substrate did not differ significantly

¹ BIOMATH, Department of Applied Mathematics, Biometrics and Process Control, Ghent University, Gent, Flanders, Belgium.

² Department of Chemical and Biochemical Engineering, Technical University of Denmark Lyngby, Copenhagen, Denmark.

³ UNESCO-IHE for Water Education, Delft, South Holland, The Netherlands.

⁴ Vitens Fryslân, Leeuwarden, Friesland, The Netherlands.

⁵ Norit Process Technology B.V., Enschede, Overijssel, The Netherlands.

⁶ modelEAU, Département de génie civil, Pavillon Pouliot, Université Laval, Québec City, QC, Canada.

^{*} Currently at ENVIRON China, Suite 14-E, New Hualian Mansion East Bldg, No. 755 Huaihai Road (m), Shanghai 200020, P. R. China; e-mail: tao.jiang@biomath.ugent.be.



Figure 1—Scheme of the laboratory-scale membrane bioreactor system.

between MBR and CAS processes for ammonia-oxidizing (AOB) and nitrite-oxidizing (NOB) biomass. However, the half-saturation coefficients for oxygen (K_0) exhibited a significant difference. The lower K_0 values obtained in the MBR are attributed to the smaller size of activated sludge flocs (35 µm versus 307 µm) that developed under conditions without selection pressure of settling but under increased shear-rate conditions. Hence, floc size characteristics imply a lower substrate diffusion limitation for MBR sludge (Shanahan and Semmens, 2006).

Jiang et al. (2005) have reported that decay rates of both heterotrophic and autotrophic biomass in a completely aerated MBR ($b_{het} = 0.25 \text{ 1/d}$ and $b_{aut} = 0.080 \text{ 1/d}$, at 23°C) are less than the default ASM1 parameter values ($b_{het} = 0.40 \text{ 1/d}$ and $b_{aut} = 0.12 \text{ 1/d}$, at 20°C) (Henze et al., 2000). Hence, care should be taken in calibrating the biomass decay rates, which can significantly affect biomass concentration.

These experimental studies suggest that replacing the secondary clarifier with a membrane leads to some differences compared to CAS systems. Thus, MBR modeling may differ from CAS modeling. Understanding these differences may help develop good modeling practices for MBR systems. The aim of this study was to investigate differences in ASM modeling approaches for MBR and CAS systems. In particular, three issues were addressed: 1) accumulation of SMP; 2) mathematical modeling of the membrane unit including backwashing and relaxation; and 3) kinetics of MBR biomass. To this end, an MBR model was built using the ASM2d and calibrated to describe the biological COD and nutrient removal in a laboratory-scale MBR (Henze et al., 2000).

Methods and Materials

A side-stream laboratory-scale MBR system was built and operated (Figure 1). A synthetic wastewater was used as influent (Boeije et al., 1999). To challenge the MBR capability in biological nutrient removal, the COD:nutrient ratio was set at less than real municipal wastewater (COD:N:P = 100:13.7:2.76). The influent flow rate was 108 L/d. The hydraulic retention time (HRT), total solids retention time (SRT), and aerobic SRT were controlled at

6.4 hours, 17 days, and 7.2 days, respectively. The bioreactor was divided into an anaerobic (8 L) and an aerobic/anoxic compartment (17 L). Alternating aeration (17 minutes aerobic conditions with dissolved oxygen concentration from 1.5 to 2.5 mg/L and 23 minutes anoxic mixing without aeration) was applied in the aerobic/anoxic compartment for nitrification and denitrification. Sludge recirculation from the aerobic/anoxic to the anaerobic compartment [0.6 L/min, 8 × Q_{in} (influent flow rate)] was applied during the last 12 minutes of the anoxic phase to reduce the recycled nitrate concentration.

The sludge in the aerobic/anoxic compartment was pumped (0.375 L/min, $5 \times Q_{in}$) to a tubular ultra-filtration membrane module for biomass separation. The PVDF (polyvinylidene fluoride) membrane is manufactured by X-Flow, The Netherlands [membrane surface area = 0.17 m²; normalized pore size = 0.03 µm (200 kDa); tube diameter = 5.2 mm; and length = 1 m]. The membrane module was operated under airlift and inside-out mode, and both cross-flow velocities for the feed sludge and air were controlled at 0.5 m/s. For every 7.5 minutes of filtration at 31.8 L/(m² · h), the membrane was backwashed for 18 seconds at 106 L/(m² · h) and relaxed for 7 seconds. The whole bioreactor and the membrane module were maintained at constant temperature (15°C) and operated over 1 year to reach steady state conditions (lasted for four months).

The separation of sludge water (soluble and colloidal component) from the whole activated sludge was performed by centrifugation (534 g) followed by membrane filtration (Millex 0.45 μ m PVDF filter, Millipore, Billerica, Massachusetts). Effluent COD, NH₄⁺-N, NO₃⁻-N, NO₂⁻-N, and total nitrogen concentrations were measured daily using colorimetric methods (HACH LANGE, Düsseldorf, Germany). The MLSS and mixed-liquor volatile suspended solids (MLVSS) concentrations were measured twice per week (American Public Health Association, 1998). The BOD was measured using an Oxitop (WTW, Germany) at 20°C. Proteins were measured using the Lowry method (Lowry et al., 1951), and polysaccharides were measured using the phenol method (Dubois et al., 1956) with corrections for nitrate interference. Volatile fatty acids (VFA) defined here as the sum of VFA with 6 or less carbon atoms—was analyzed with a capillary flame ionization detector gas chromatograph (8000 Carlo Erba Instruments, Wigan, United Kingdom). The LC-OCD analysis was performed by a commercial laboratory (DOC-LABOR, Germany) (Huber and Frimmel, 1991).

To help develop and calibrate the model, a measurement campaign was done to capture the in-cycle dynamics, such as phosphate release and uptake, nitrification, and denitrification because of the alternating aeration and periodical recirculation. Samples were taken from the three compartments every 5 to 17 minutes during a 40-minute cycle.

A respirometer (2 L) controlled for temperature (15°C), dissolved oxygen (3 to 4 mg/L), and pH (7.5 \pm 0.2) was used to determine sludge oxygen uptake rate (OUR). The respirometer was equipped with a dissolved oxygen sensor (Mettler Toledo, Inpro 6400) and a pH sensor (Mettler Toledo HA 405-DXK-S8/225). The OUR was estimated from the linear part of the dissolved oxygen decline profile using linear regression when aeration was switched off.

The decay rate of the autotrophic biomass (b_{aut}) was determined from batch respirometer experiments (Spanjers and Vanrolleghem, 1995). Alternating aeration (49.4 minutes aerobic conditions with dissolved oxygen concentration from 1.5 to 2.5 mg/L and 70.6 minutes anoxic mixing without aeration) was used to keep the same aerated and nonaerated mass ratio as that of the laboratory-scale MBR. The sludge was spiked daily with ammonium chloride ($S_{NH4}/X_0 = 0.0005$). The measured OUR was corrected by estimating the new biomass produced by the spiked substrate; nonlinear curve fitting was used to estimate the decay rate.

LabVIEW (National Instruments, Austin, Texas) was used for automated data acquisition and process control. The WEST simulation software (MOSTforWATER NV, Kortrijk, Belgium) was used for model building, simulations and parameter estimations. The BIOMATH and STOWA protocols (developed for CAS systems) were used as guidelines to help develop a good model, and the differences between MBR and CAS modeling have been highlighted (Vanrolleghem et al., 2003; Roeleveld and van Loosdrecht, 2002).

Results and Discussion

Data Quality Check and Steady State Mass Balance. To check the experimental data quality under steady-state conditions, mass balances of phosphorus and nitrogen were verified using the method of Ekama et al. (1986). The amount of denitrified nitrate and nitrite was estimated from mass balance over the anaerobic compartment and the anoxic phase of the aerobic/anoxic compartment using the measurement campaign results (Table 1). The overall mass balance showed that only 0.42% phosphorus and 2.05% nitrogen were lost, which is an indication of good data quality and correct control of sludge age (Meijer et al., 2002; Nowak et al., 1999).

Accumulation of Soluble Microbial Products. The sludge and effluent characteristics of MBR under steady-state conditions are summarized in Table 2. Excellent COD removal was achieved (97.6%). The Soluble COD (through 0.45 μ m filter) in the permeate (11.0 mg/L) was significantly lower than in the sludge water (87.4 mg/L in the aerobic/anoxic compartment and 107.4 mg/L in the membrane feed side). This result suggests that Soluble COD (SCOD) in the MBR wastewater was not truly soluble but contained a large portion of colloidal and macromolecular organic compound. It also suggests that the wastewater was composed primarily of SMP, which were retained by the ultrafiltration membrane. Finally, it suggests that SMP in MBR wastewater were refractory, because

| Table 1- | -Steady-state | mass bala | ance of | phosphorus | and |
|----------|----------------|-----------|----------|----------------|-----|
| nitroaen | (TP = total p) | hosphorus | : TN = 1 | total nitroger | ı). |

| Phosphorus mass bala | ince | Nitrogen mass balance | | | |
|------------------------|-------|------------------------|-------|--|--|
| TP in the influent | 1351 | TN in the influent | 6774 | | |
| TP in the effluent | 1001 | TN in the effluent | 0114 | | |
| (mg P/day) | 618 | (mg N/day) | 1083 | | |
| TP in the waste sludge | | TN in the waste sludge | | | |
| (mg P/day) | 727 | (mg N/day) | 1286 | | |
| | | Nitrate denitrified | | | |
| | | (mg N/day) | 4265 | | |
| Loss of TP | 0.42% | Loss of TN | 2.05% | | |

the BOD values were so low (BOD₅ = 1.7 and BOD₁₇ = 4.6 mg/L), which resulted in a low BOD₅/COD ratio (0.019) (Daigger and Grady, 1977; Grady et al., 1972).

In view of MBR modeling, it becomes clear that SMP is an important system component for consideration. Further, as this COD fraction is not defined in ASM2d, the closing of COD mass balance will be an important issue. Because this study focuses only on biological nutrient removal, a complicated extension of ASM2d with SMP was avoided. A pragmatic, yet simple solution was used in this study, in which the SMP was treated as inert particulate COD (X_I) because of their refractory and retainable characteristics. It is, however, important to emphasize that for modeling membrane fouling, SMP should be considered explicitly as an additional COD component as done in other studies (Lu et al., 2001; Lu et al., 2002; Jiang et al., 2008).

Biological Nutrient Removal Effect of MBR Configuration and Operation. Removal of total nitrogen and phosphorus was 83.7% and 49.3%, respectively. The unsatisfactory enhanced biological phosphorus removal (EBPR) suggests that the heterotrophic biomass obtained a competitive advantage over phosphorus accumulation organisms (PAO) for volatile VFA uptake. This was because of (1) the challenging influent characteristics (low COD: nutrient ratio and contained 6.5 mg O₂/L and 2.94 mg NO₃-N/L); and (2) an inappropriate compartment configuration (Figure 3). A combined aerobic/anoxic compartment with alternating aeration was used because of the limitation of experimental budge. As a result of using air for membrane fouling control, a high flow rate $(4 \times Q_{in})$ of rejected sludge containing 6 mg O₂/L was introduced into the anoxic zone. Thus, denitrification was incomplete and 0.7 to 2 mg NO₃-N/L was returned to the anaerobic compartment, hindering good EBPR performance.

Separating aerobic and anoxic compartments and returning rejected sludge flow from membranes to the aerobic compartment are therefore essential for MBRs. Typical rejected sludge flow contains a high dissolved oxygen, whereas the secondary clarifier underflow in CAS processes contains a much lower dissolved oxygen. Thus, the rejected sludge flow from membranes is more suitable to be returned to an aerobic zone; whereas, returning the clarifier underflow to an anoxic or anaerobic zone is a common practice (for example, Phoredox, A²O, and University of Cape Town process).

Hydraulic Model. Tracer tests were performed to check mixing conditions in the anaerobic compartment. Sodium chloride was used as tracer, and conductivity was measured every second. The conductivity measurements were converted to sodium chloride concentration using a calibration curve. Three types of tracer tests (pulse, step-up, and step-down) showed that sodium chloride

Table 2—Comparison of measurements and model simulation results under steady-state conditions (COD = chemical oxygen demand; BOD = biological oxygen demand; MLSS = mixed-liquor suspended solids; MLVSS = mixed-liquor volatile suspended solids; S_A = fermentation products/substrate; S_{NO3} = nitrate nitrogen; S_{NO2} = nitrite nitrogen; S_O = dissolved oxygen; S_{NH4} = ammonium plus ammonia nitrogen; S_{TN} = soluble total nitrogen; S_{TP} = soluble total phosphorus).

| | | Values | | | | |
|---|---|--|--|----------------------------------|----------------------------------|--|
| Sample (sampling location) | Unit | 4-month average | Standard deviation | Simul_1 | Simul_2 | |
| Waste sludge (from aerobic/anoxic compartment) | MLSS (g/L) MLVSS (g/L) MLVSS/MLSS COD (g/L) COD/MLVSS | 8.86 7.47 0.84 10.90 1.46 | 1.13 0.72 0.65 | 10.83 | 10.94 | |
| Sludge water (separated waste sludge using 0.45 µm) | Polysaccharides (mg/L) Proteins (mg/L) COD (mg/L) BOD ₅ (mg/L) BOD ₁₇ (mg/L) | 32.8 13.8 87.4 1.7 4.6 | 6.8 4.1 22.7 | 4.5 | 4.1 | |
| Effluent (from permeate) | COD (mg/L) S _{TN} (mg/L) S _{NH4} (mg/L) S _{NO3} (mg/L) S _{NO2} (mg/L) S _{TP} (mg/L) | 11.0 (97.6%) 10.2 (83.7%) 0.18 7.0 0.30 5.8 (49.3%) | 3.1 2.8 0.42 1.7 0.21 2.2 | 5.0 8.8 0.18 8.6 5.4 | 4.4 8.0 0.20 7.8 5.7 | |

¹ The values in parenthesis are removal percentage.

² Simul_1 = Simulation using a complete membrane model describing the discontinuity of backwashing/relaxation.

³ Simul_2 = Simulation using a simple membrane model that normalizes the discontinuity.

recoveries were in the range of 0.877 to 1.03. A comparison of model simulations (using one and two-tank in series model) and measurements for the step-down test is shown in Figure 2. It is evident that a completely mixed reactor is the best hydraulic model for the anaerobic compartment. The aerobic/anoxic compartment and the feed side of the membrane loop should have better mixing

conditions because of aeration. Thus, the two bioreactor compartments together with the feed side of the membrane loop can be described as completely mixed reactors (Figure 3).

Mathematical Description of the Membrane Unit. The periodic membrane backwashing/relaxation resulted in discontinuity in the effluent flow, which is a unique feature of MBR operation.



Figure 2—Comparison of simulated sodium chloride (NaCl) concentrations using one- and two-tank in-series model with measurements (step-down test).



Figure 3—Mode of the membrane bioreactor configuration (dashed line is backwashing in complete hydraulic model).

A complete model description of backwashing/relaxation is complex. Normalizing the discontinuity of backwashing/relaxation and describing the membrane as a simple continuous flow-through point separator will generate errors; the magnitude of these errors has not been studied yet. To address this question, two MBR models with the same ASM2d parameters but different membrane modeling approaches were developed and compared: (1) a complete membrane model describing the periodical backwashing/relaxation; and (2) a simple membrane model that normalizes the discontinuity.

Comparison of simulation results of the two models and measurements are shown in Table 2. The complete membrane model yielded only a slight improvement in fitting the effluent nitrate and phosphate concentration. However, the simulation was three times slower. Hence, a simple membrane model that normalizes the discontinuity is acceptable.

Influent Wastewater Characterization. Typically, influent wastewater was characterized in terms of ASM2d components (Table 3) using the STOWA protocol with modification (Roeleveld and van Loosdrecht 2002). A 0.45-µm filter was used to separate soluble and particulate compounds.

Influent chemical oxygen demand components. The VFA (S_A) was measured directly using gas chromatography. The inert soluble COD (S_I) was assumed to originate primarily from the tap water, because other organics used in making the synthetic influent are readily biodegradable. Humic substances were the main source of S_I in tap water (Klavins et al., 1999). Thus, influent S_I was estimated to be 1.6 \pm 0.4 mg DOC/L by direct measure. If the DOC/COD ratio of humic substances is assumed to be 0.4, then the approximate S_I present in the MBR influent would be 4 mg COD/L. The fermentable soluble COD could then be estimated as $S_F = SCOD - S_A - S_I$.

The inert particulate COD (X_I) was assigned a value obtained previously for this wastewater (Insel et al., 2006). The simulated MLSS concentration was able to fit the measurements, which justified the influent X_I estimation. Membrane bioreactors often operate under high SRT and low HRT conditions. Thus, sludge concentration is more sensitive to influent X_I , which can be regarded as an advantage for MBR influent characterization (Jiang et al., 2005). The influent dissolved oxygen concentration (6.5 mg O₂/L) were measured directly and included in the influent characterization.

Influent nitrogen and phosphorus components. The influent ammonium concentration (S_{NH4}) was measured directly. The main nitrogen source of the synthetic wastewater was urea. However, as

soluble organic nitrogen is not defined in ASM2d, the urea nitrogen was included in S_{NH4} (the ammonification process is assumed not to be a rate-limiting step). This simplification was justified by a trial simulation, in which entrapping organic nitrogen in Xs (slowly biodegradable substrate) resulted in worse fitting of simulated effluent ammonium and nitrate with the measurements. The influent nitrate concentration (2.94 mg NO₃-N/L by direct measurements) was included in the influent characterization. The influent orthophosphate (S_{PO4}) was measured directly.

It should be noted that a synthetic influent was used in this study to maintain stable influent characteristics. Domestic sewage exhibits various characteristics and can be more complex. Synthetic influent is more stable and thus more helpful for use in studies.

Dynamic Calibration of the Model. A large part of the MBR model comprises the ASM2d model structure, which contains many parameters. In this study, the decay rate of the autotrophic biomass was obtained from batch experiments as they were found to be different for MBR systems (see the next section). Most remaining parameters were taken as the defaults from the ASM2d. A preselected parameter set was calibrated following guidelines proposed in literature (Hulsbeek et al., 2002; Insel et al., 2006). The dataset used in the dynamic model calibration includes the in-cycle

Table 3—Summary of influent characterization as activated sludge model 2d fractions (COD = chemical oxygen demand; S_I = inert soluble organic COD; S_A = fermentation products/substrate; S_{NO3} = nitrate plus nitrite nitrogen; S_O = dissolved oxygen; S_{PO4} = inorganic soluble phosphorus; S_{NH4} = ammonium plus ammonia nitrogen; S_F = fermentable soluble substrate; X_I = inert particulate organic COD; X_S = slowly biodegradable substrate; X_{TSS} = total suspended solids).

| COD fraction | | Nitrogen fr | action | Phosphorus fraction | | |
|--|---|--|---|---|----------------------------|--|
| $\begin{array}{l} S_{I} (mg/L) \\ S_{A} (mg/L) \\ S_{F} (mg/L) \\ X_{I} (mg/L) \\ X_{S} (mg/L) \\ X_{TSS} (mg/L) \\ S_{\Omega} (mg/L) \end{array}$ | 4 41.2 113 18 281 219 6.5 | S _{NH4} (mg/L) S _{NO3} (mg/L) i _{N,SI} i _{N,SF} i _{N,XI} i _{N,XS} | 46.1 2.94 0.01 0.03 0.02 0.035 | S _{PO4} (mg/L) i _{P,SI} i _{P,SF} i _{P,XI} i _{P,XS} | 11.1 0 0.01 0.005 | |
| | | | | | | |



Figure 4—Exponential decrease of corrected exogenous oxygen uptake rate in b_{aut} determination.

dynamic data obtained from the measurement campaign and fourmonth average steady-state results.

Decay Rate for Autotrophic Biomass. A batch experiment was performed to estimate the decay rate of autotrophic biomass (b_{aut}). The exponential decrease of the corrected exogenous OUR is presented in Figure 4. The obtained b_{aut} was low (0.031 ± 0.004 1/d) at 15°C. Using the default temperature conversion factors ($\theta = 1.116$) in ASM2d, the decay rate at 20°C was estimated to be 0.055 ± 0.005 1/d, which is still significantly lower than the default ASM2d value (0.15 1/d).

However, it should be noted that this low decay value was obtained under alternating aeration conditions. Anoxic decay rate can be significantly lower than aerobic decay rate. Manser et al. (2006) has reported that the aerobic decay rates of AOB, NOB, and heterotrophic bacteria for CAS and MBR systems were not significantly different. However, anoxic decay rates were 4 to 14 times lower than the aerobic decay rates. If $b_{aut,aero} = 0.15 \text{ 1/d}$ and $b_{aut,anoxic} = 0.015 \text{ 1/d}}$ are assumed, then the decay rate under this alternating aeration condition is estimated to be 0.071 1/d, which is close to the value observed in this study, 0.055 1/d (Manser et al., 2006).

Decay Rate for Heterotrophic Biomass. A simulation with the ASM2d default b_{het} value (0.4 1/d) resulted in a total sludge COD concentration of 10.83 g/L in the aerobic compartment, which is in agreement with the measured value (10.90 g/L). Thus, the default b_{het} value was adopted without adjustment.

Experience and Process-Knowledge Based Model Calibration. 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 parameters of the model. The calibrated parameters were then transferred to the next step.

A simulation with default parameter values overestimated the effluent ammonium concentration. The nitrification activity should, therefore, be improved; thus, the oxygen half-saturation coefficient for autotrophic biomass ($K_{O,aut}$) was reduced from 0.5 to 0.2 mg/L. Manser et al. (2005a) have reported $K_{O,AOB} = 0.18 \pm 0.04$ mg O_2/L and $K_{O,NOB} = 0.13 \pm 0.06$ mg O_2/L in a pilot MBR. They attributed the high oxygen affinity to the small floc sizes (35 µm of the 50% percentile) and the reduced oxygen diffusion limitation. The mean floc size in this MBR was only 30 to 50 µm, which justified the low diffusion limitation.

However, the decrease in K_{O,aut} was not sufficient to reduce the ammonium concentration to the measurement values. The ammonium half-saturation coefficient (K_{NH4,aut}) was therefore decreased as well, from 1 to 0.2 mg N/L. A low K_{NH4,aut} of MBR sludge is also consistent with the findings of Manser et al. (2005a) (K_{NH4} = 0.13 \pm 0.05 mg N/L and K_{NO2} = 0.17 \pm 0.06 mg N/L).

The simulation overestimated nitrate concentration and underestimated phosphorus concentration, which suggests that more VFA should be used in denitrification by ordinary heterotrophic biomass rather than for poly-hydroxy-alkanoate (PHA) formation by phosphorus accumulating organisms (PAO). After some trial and error using process insight, $\eta_{NO3,het}$, q_{PHA} , q_{fe} , q_{pp} and $\eta_{NO3,PAO}$ were adjusted (Table 4).

Typically, the model was able to follow the reactor in-cycle dynamics (Figure 5) and the root mean squared error (RMSE) of the different fits were less than 1.2 mg/L except for the VFA (Table 5). In the anaerobic compartment, the ammonium, nitrate, and phosphate fitting were good because they followed the measured pattern. However, the measured VFA showed no pattern, which was probably because the measured VFA concentrations (2 to 4 mg/L) were lower than the gas chromatography detection limit (10 mg/L). The ammonium, nitrate, and phosphate fitting in the aerobic compartment were not good, which might be related to the small concentration dynamics and the difficulty in taking representative samples in short cycle times (40 minutes).

The higher affinity (lower half-saturation coefficient) of oxygen and ammonium uptake and the lower maximum specific growth rate

Table 4—Summary of calibrated activated sludge model 2d parameters (20°C) [b_{aut} = decay rate of nitrifiers; μ_{aut} = maximum specific growth rate of nitrifiers; $K_{O,aut}$ = oxygen half-saturation coefficient of nitrifiers; K_{NH4} = ammonium half-saturation coefficient; q_{fe} = fermentation rate of acetate production; q_{PHA} = poly-hydroxy-alkanoate storage rate; q_{pp} = phosphate uptake rate; $\eta_{NO3,het}$ = reduction factor of anoxic growth of heterotrophs (-); $\eta_{NO3,PAO}$ = Reduction factor of anoxic growth of PAO (-)].

| Parameter name | Symbol | Unit | Default | Calibrated |
|--|----------------------|----------------------|---------|------------|
| Decay rate of nitrifiers | b _{aut} | 1/d | 0.15 | 0.055 |
| Maximum specific 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 _{NH4.aut} | mg N/L | 1 | 0.2 |
| Reduction factor of anoxic growth of heterotrophs | η _{NO3.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 | Qpp | 1/d | 1.5 | 1.1 |
| Reduction factor of anaerobic hydrolysis | $\eta_{NO3,PAO}$ | — | 0.6 | 0.4 |



Figure 5—Comparison of the simulation and measurement data of the in-cycle behavior (aerobic = aerobic phase; anoxic mixing = anoxic phase without recirculation; anoxic recirculation = recirculating sludge from anoxic compartment to anaerobic compartment; DO = dissolved oxygen).

of MBR autotrophic biomass seems consistent with the hypothesis that complete sludge retention in an MBR changes the selection pressure on the biomass population from the sludge settling properties (in CAS) to growth kinetics (in MBR). A practical consequence can be deduced as follows. If the same nitrification rate is maintained for MBR and CAS sludge, then a sudden increase in influent ammonium loading will not significantly increase MBR nitrification rates because the nitrifiers are maximum growth rate limited. However, nitrifiers in CAS are affinity limited, which maintains the capacity of increasing nitrification rate because of elevated ammonium concentration. For process designers, the nitrification in MBRs should, therefore, be designed more conservatively compared to that in CAS systems.

Effect of Soluble Microbial Products on Autotrophic Biomass. The MBR sludge exhibited a lower specific growth rate in the dynamic model calibration, which might be related to the high SMP concentration in the MBR wastewater. It has been reported that SMP inhibit nitrification and anaerobic acetate uptake of PAO in CAS

Table 5—Root mean squared error (RMSE) values in fitting measurement campaign results (S_A = fermentation products/ substrate; S_{NO3} = nitrate plus nitrite nitrogen; S_O = dissolved oxygen; S_{PO4} = inorganic soluble phosphorus; S_{NH4} = ammonium plus ammonia nitrogen).

| | Anaerobic | | | Aerobic/anoxic | | | | |
|-------------|----------------------|------------------|------------------|------------------|------|------------------|------------------|------------------|
| | S _A (VFA) | S _{NO3} | S _{PO4} | S _{NH4} | So | S _{NO3} | S _{PO4} | S _{NH4} |
| RMSE (mg/L) | 2.68 | 0.17 | 0.95 | 1.02 | 0.21 | 0.49 | 1.18 | 0.43 |

systems (Ichihashi et al., 2006; Chudoba, 1985). To evaluate the effect of SMP on nitrification in MBRs, two comparative nitrification batch tests were conducted.

Washed sludge with a reduced SMP (SCOD = 24 versus 86 mg COD/L) showed a slightly lower endogenous respiration rate $[0.57 \pm 0.01 \text{ versus } 0.60 \pm 0.01 \text{ mgO}_2/(L \cdot \text{min})]$ than the raw sludge, which was expected because of the loss of unflocculated sludge during washing. However, the washed sludge exhibited a higher exogenous respiration rate $[0.69 \pm 0.07 \text{ versus } 0.62 \pm$ $0.06 \text{ mgO}_2/(L \cdot \min)$ spiked by ammonium] than the raw sludge, suggesting that nitrifiers were more active at reduced SMP concentration conditions. Soluble microbial products can accumulate to a higher concentration in MBRs than that in CAS systems because of membrane retention. Therefore, care should be taken in design and operation of MBRs under high SRT conditions, because longer SRT conditions can cause significant SMP accumulation (Jiang et al., 2008). However, standard deviations of these two batch tests were high. Therefore, further studies are recommended to address this topic, such as nitrification rate at different SMP concentrations.

Current Limitations of the Models and Future Perspective. The experience-based, manual trial-and-error approach used to calibrate many activated sludge models was found to be useful for MBR models as well (Sin et al., 2008). Other CAS model calibration experience, such as the importance of influent characterization, nitrification kinetics, mixing, and sludge balance, are also valid for MBR model applications.

Limitations of MBR models—such as effects of SMP on the membrane fouling, inhibitory effects of SMP accumulation on nitrification, and mass transfer related to membrane operation need further study and clarifications. In addition, configurations, membrane types, cleaning methods, and operational parameters vary among commercially available MBRs. As a result, activated sludge characteristics vary in composition and size from system to system. This variability can result in different physiological behavior of nitrifiers affecting growth and decay kinetics, which has important implications for MBR design. Therefore, more process characterization and modeling studies are needed for a range of different MBR systems to provide guidelines for MBR modeling.

Conclusions

A laboratory-scale MBR exhibited excellent COD removal, good nitrogen removal, but poor phosphorus removal in treating a high nutrient content synthetic wastewater. There are, however, several issues that need to be considered for a better mechanistic modeling of MBR systems:

- A lower maximum specific growth rate for MBR nitrifiers was estimated. Independent experiments demonstrated that this might be attributed to the inhibition effect of SMP at elevated concentration. Consequently, ASM extension with SMP are required not only to predict MBR fouling, but for better description of the nitrification process.
- The MBR biomass exhibited a higher affinity to oxygen and ammonium probably because of smaller sludge flocs, which is less diffusion limited.
- Finally, the membrane throughput during membrane backwashing/relaxation can be normalized and the membrane can be modeled as a continuous flow-through point separator. This simplicity has only a minor effect on ASM simulation; however, it significantly improved simulation speed.

A tubular membrane operated at fixed airlift mode was modeled in this study. However, commercially available MBRs vary in configurations, membrane types, and hydrodynamic conditions. Each MBR system can, therefore, have unique sludge characteristics, biomass physiology, and consequent effect on MBR modeling. More process characterization and modeling studies similar to the ones conducted in this study are needed.

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Nomenclature

AOB = Ammonia-oxidizing biomass

- ASM = Activated sludge model
 - b_{aut} = Decay rate of nitrifiers (1/d)
- $b_{het} = Decay rate of heterotrophs (1/d)$
- BOD = Biochemical oxygen demand
- CAS = Conventional activated sludge
- COD = Chemical oxygen demand
- DOC = Dissolved organic carbon
- EfOM = Effluent organic matter
- HRT = Hydraulic retention time
- $K_La = Oxygen transfer coefficient$
- K_{NH4} = Ammonium half-saturation coefficient (mg N/L)
- K_{O} = Oxygen half-saturation coefficient (mg O₂/L)
- $K_{O,aut} = Oxygen$ half-saturation coefficient of nitrifiers
- LC-OCD = Liquid chromatography-organic carbon detection
 - MBR = Membrane bioreactor
 - MLSS = Mixed-liquor suspended solids
- MVLSS = Mixed-liquor volatile suspended solids
 - NOB = Nitrite-oxidizing biomass
 - NOM = Natural organic matter
 - OUR = Oxygen uptake rate
 - PAO = Phosphorus accumulating organism
 - PHA = Poly-hydroxy-alkanoate
 - q_{fe} = Fermentation rate of acetate production (1/d)
 - $Q_{in} =$ Influent flow rate
 - $q_{PHA} = PHA$ storage rate (1/d)
 - q_{pp} = Phosphate uptake rate (1/d)
- RMSE = Root mean squared error
- S_A = Fermentation products/substrate (mg COD/L) SCOD = Soluble COD
- $= \sqrt{1}$ = E-meantable columbia
- S_F (mg/L) = Fermentable soluble substrate (mg COD/L)
 - S_{I} = Inert soluble organic COD (mg COD/L)
 - SMP = Soluble microbial products
 - S_{NH4} = Ammonium plus ammonia nitrogen (mg N/L)
 - S_{NO3} = Nitrate plus nitrite nitrogen (mg N/L)
 - S_{O} = Dissolved oxygen (mg O_2/L)
 - S_{PO4} = Inorganic soluble phosphorus (mg P/L)

- SRT = Solid Retention Time (1/d)
- S_{TN} = Soluble total nitrogen (mg N/L)
- S_{TP} = Soluble total phosphorus (mg P/L)
- VFA = Volatile fatty acids
- $X_I (mg/L) = Inert particulate organic COD (mg COD/L)$
- X_{S} (mg/L) = Slowly biodegradable substrate (mg COD/L)
 - X_{TSS} = Total suspended solids (mg/L)
- $\eta_{NO3,het}$ = Reduction factor of anoxic growth of heterotrophs (-) $\eta_{NO3,PAO}$ = Reduction factor of anoxic growth of PAO (-)
 - μ_{aut} = Maximum specific growth rate of nitrifiers (1/d)

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