Modeling of extracellular polymeric substances and soluble microbial products production in a submerged membrane bioreactor at various SRTs

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Abstract Extracelluar polymeric substances (EPSs) and soluble microbial products (SMPs) produced by microbial cultures involved in membrane biofouling have been widely investigated. A mathematical model of EPS and SMP formation and degradation was established based on the activated sludge model no. 1 (ASM1) and was applied to the membrane bioreactor sludge with different sludge retention times (SRTs). The unified theory that the distinct products from the EPS and SMP overlapped each other was integrated into the ASM1. Two components, five processes and eight parameters were newly added to set up the model. To increase the accuracy of model simulation, microbial kinetic parameters were determined by respirometry method and applied to the model instead of microbial kinetic constant offered in ASM1. From the respirometry result, both of heterotroph and autotroph showed different yield value, growth rate and decay rate from activated sludge. There was no significant effect of SRT on SMP production and the experimental results showed good agreement with the predicted values by the model simulation. With the developed unified EPS and SMP model, EPS and SMP production could be simulated so well that it can be applied for the membrane biofouling control.

Keywords Extracellular polymeric substance; model simulation; soluble microbial product

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Nomenclature

b_A	autotrophic decay coefficient for formation of particulate, day^{-1}
b_H	heterotrophic decay coefficient for formation of particulate, day^{-1}
f_P	inert fraction of biomass leading to particulate products, dimensionless
i_{XB}	mass N/mass COD in biomass, gN $gCOD^{-1}$
i_{XP}	mass N/mass COD in products from biomass, gN $gCOD^{-1}$
K_a	ammonification coefficient, m^3 $gCOD^{-1}$ day^{-1}
k_{BAP}	hydrolysis coefficient of EPS, day^{-1}
k_{EPS}	EPS formation coefficient by heterotrophs, dimensionless
k_{EPSa}	EPS formation coefficient by autotrophs, dimensionless
K_h	hydrolysis coefficient, day^{-1}
k_{UAP}	UAP formation rate coefficient of heterotrophs, dimensionless
k_{UAPa}	UAP formation rate coefficient of autotrophs, dimensionless
K_{NH}	ammonia half-saturation coefficient for autotrophic biomass, gN m^{-3}
K_{NO}	nitrate half-saturation coefficient for denitrifying heterotrophs biomass, gN m^{-3}
$K_{O.A}$	oxygen half-saturation coefficient for autotrophs, gO_2 m^{-3}
$K_{O.H}$	oxygen half-saturation coefficient for heterotrophs, gO_2 m^{-3}
K_S	substrate half-saturation coefficient for heterotrophs, gCOD m^{-3}
K_{SMP}	SMP half-saturation coefficient for heterotrophs, gCOD m^{-3}

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K_X	half-saturation coefficient for hydrolysis of particulate biodegradable substrate, dimensionless
K_{XEPS}	half-saturation coefficient for hydrolysis of EPS, dimensionless
S_{BAP}	biomass-associated product, gCOD m^{-3}
S_I	soluble inert organic matter, gCOD m^{-3}
S_{NDSS}	soluble biodegradable organic nitrogen, gN mV
S_{NH}	ammonia plus ammonium nitrogen, gN m^{-3}
S_{NO}	nitrate plus nitrite nitrogen, gN m^{-3}
S_O	oxygen, gO_2 m^{-3}
S_S	soluble biodegradable substrate, gCOD m^{-3}
S_{SMP}	total soluble microbial product, equals to S_{BAP} plus S_{UAP}, gCOD m^{-3}
S_{UAP}	utilization associated product, gCOD m^{-3}
$X_{B.A}$	active autotrophs, gCOD m^{-3}
$X_{B.H}$	active heterotrophs, gCOD m^{-3}
X_{EPS}	particulate EPS, gCOD m^{-3}
X_I	particulate inert organic matter, gCOD m^{-3}
X_{ND}	particulate biodegradable organic nitrogen, gN m^{-3}
X_P	particulate products from biomass decay, gCOD m^{-3}
X_S	particulate biodegradable organic matter, gCOD m^{-3}
Y_A	autotrophic yield coefficient, gCOD gN^{-1}
Y_H	heterotrophic yield coefficient from substrate, gCOD gCOD − 1
Y_{SMP}	heterotrophic yield coefficient from SMP, gCOD $gCOD^{-1}$
η_g	correction factor for anoxic growth of heterotrophs, dimensionless
η_h	correction factor for anoxic hydrolysis, dimensionless
μ_A	maximum specific growth rate for autotrophs, day^{-1}
μ_H	maximum specific growth rate for heterotrophs, day^{-1}
μ_{SMP}	maximum specific growth rate of SMP for heterotrophs, day^{-1}
ρ	process rate, gCOD m^{-3} day^{-1} or gN m^{-3} day^{-1}

Introduction

In recent years, membrane filtration has been increasingly used with the activated sludge bioreactors in conventional wastewater treatment to achieve higher effluent quality (Bai and Leow, 2002). The major obstacle in the extensive use of membrane bioreactor is membrane fouling, characterized by a rapid and continuous reduction of permeation flux with time, which has commonly been attributed to the high concentrations of suspended solids in wastewater (Zeman and Zydney, 1996). In addition to mixed liquor suspended solids, EPSs and SMPs are known as main microbial products to induce the membrane bio-fouling. EPS is accumulated in the bioreactor and also on the membrane, which cause an increase of viscosity of the mixed liquor and an increase in the filtration resistance (Nagaoka *et al.*, 1996). Also high molecular SMP which is larger than the molecular weight cut-off (MWCO) of the ultrafiltration membrane can not penetrate membrane pores due to size exclusion which could act as a foulant in MBR processes (Shin and Kang, 2003).

A model incorporating EPS and SMP formation and degradation may offer a rational approach to the biofouling characteristics of the membrane bioreactor process. Therefore, the objective of this study is to establish an available model by incorporating the unified EPS and SMP concept into the membrane bioreactor process in order to accurately predict their fate under various SRT conditions.

Materials and methods

Membrane bioreactor operation

As shown in Figure 1 and Table 1, three submerged membrane bioreactors having 17 L of working volume were operated under different SRT conditions. The microfiltration membrane was made of polypropylene having a nominal pore size of 0.4 μm and an effective filtration area of 0.1 m^2. Initially, the bioreactor was filled with sludge from a municipal wastewater treatment plant. MBR reactors were fed with the synthetic wastewater containing glucose and ammonia as carbon and nitrogen sources. Influent COD and nitrogen concentrations were fixed at 180 mg/L (0.37 kg COD/m^3/d) and 30 mg/L (0.06 kg NH_4-N/m^3/d), respectively.

Analytical methods

Suspended solids (SS), COD, and NH_4-N concentrations were measured according to *Standard Methods* (APHA, 1998). Concentrations of various ions in solution were analyzed using ion chromatography (DX-120, DIONEX, USA). Total organic and inorganic carbons were determined by a TOC analyzer (DC-180, Dorhmann, Germany). EPS was extracted from microbial floc using heat treatment (Morgan *et al.*, 1990). The extracted solution was analyzed for total carbohydrate and proteins. The amounts of total carbohydrates and proteins represented the EPS, as they are dominant components typically found in extracted EPS (Bura *et al.*, 1998; Frølund *et al.*, 1996). Carbohydrates and proteins in EPS were determined according to the phenol-sulfuric acid method with glucose as standard (Dubois *et al.*, 1956) and Folin method with bovine serum albumin as standard (Lowry *et al.*, 1951), respectively. The SMP concentration could be estimated using the biodegradable organic matter (BOM) removal (as carbon), the DOC removal and the SMP biodegradation as in Equation (1). BOM removal represents the consumption of the influent substrate (glucose) that should be equal to the DOC removal if no SMP presented. If SMP presented, the DOC removal would be reduced by the amount of SMP produced (Shin and Kang, 2003).

$$\begin{aligned} \mathrm{SMP} &= \mathrm{BOM}_{\mathrm{removal}} - \mathrm{DOC}_{\mathrm{removal}} + \mathrm{SMP}_{\mathrm{biodegradation}} \\ &= (\mathrm{BOM}_{\mathrm{influent}} - \mathrm{BOM}_{\mathrm{effluent}}) - (\mathrm{DOC}_{\mathrm{influent}} - \mathrm{DOC}_{\mathrm{effluent}}) + \mathrm{SMP}_{\mathrm{biodegradation}} \end{aligned} \quad (1)$$

Kinetic parameter determination

The respirometer used for parameter estimation was AER-200/ANR-100 system (Challenge Environmental System, Inc.), which measures the oxygen transfer rate into the sludge. Sludge was taken out and washed twice to remove the residual COD and nitrate.

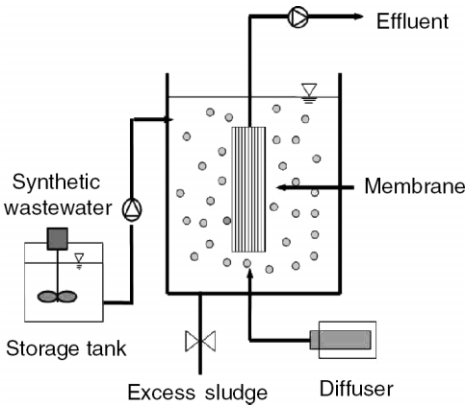

Figure 1 Schematic diagram of MBRs

Table 1 Operating conditions of MBRs

Category	R1	R2	R3
COD/N ratio		6	
SRT (days)	30	60	90
HRT (hr)		8.0	
Permeate flux (LMH)		21.3	
Max. TMP (kPa)		26.7	
Air flow rate (L/min)		2.0	
Organic loading (kgCOD/m^3/day)		0.37	
pH		7.0 ± 0.2	
DO (mgO_2/L)		>2	

And then the alkalinity and phosphate were supplied to avoid the pH drop and nutrient deficiency. Finally the sludge was aerated for 30 min to confirm the endogenous stage (Figure 2). Three major parameters including yield, growth rate and decay rate were estimated with respirometry suggested by Vanrolleghem *et al.* (1999).

Model development

EPS and SMP formation-degradation was simulated with a mathematical model based on the activated sludge model no. 1 (ASM1). In this model, a unified theory that the distinct products from the EPS and SMP were overlapped each other, was used (Figure 3). EPS and SMP formation can be expressed with the following Equation (2) and (3), respectively (Characklis and Marshall, 1990; Rittman and McCarty, 2001).

$$r_{EPS} = k_1 \mu X + k_2 X \tag{2}$$

$$r_{SMP} = k_{UAP} q X + k_{BAP} X \tag{3}$$

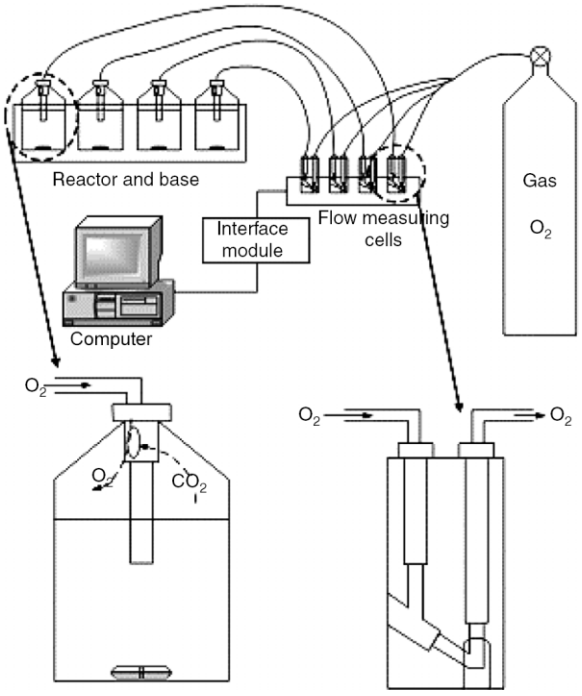

Figure 2 Schematic diagram of respirometry

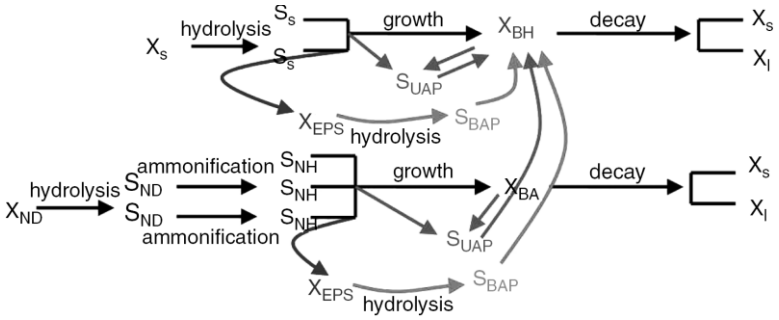

Figure 3 Schematic representation of EPS and SMP production and degradation

To set up the EPS and SMP model, new components of S_{SMP}, and X_{EPS} were added. S_{SMP} is the soluble biodegradable SMP concentration and X_{EPS} is slowly biodegradable EPS concentration in wastewater. For the process modeling, five processes were added: hydrolysis of EPS, EPS formation by heterotrophs, EPS formation by autotrophs, UAP formation by heterotrophs, and UAP formation by autotrophs. To describe the newly added processes, eight parameters used were μ_{SMP}, k_{UAP}, k_{UAPa}, k_{BAP}, K_{SMP}, k_{EPS}, k_{EPSa}, and K_{XEPS}. Based on above statement, the mass balance equation including the EPS and SMP concept was established as shown in Table 2.

Results and discussions

Sensitivity analysis of parameters

In order to determine the major parameters, sensitivity analysis was made. Eighteen kinetic parameters associated with SMP and EPS were selected for analysis.

As shown in Figure 4, the most important factors affecting the EPS production were BAP formation coefficient (k_{BAP}), EPS formation coefficient (k_{EPS}), and decay coefficient for heterotrophic biomass (b_H). Maximum specific growth rate of SMP for heterotrophs (μ_{SMP}), heterotrophic yield coefficient from SMP (Y_{SMP}), and SMP half-saturation coefficient for heterotrophic biomass (K_{SMP}) had great influences on the SMP production.

Table 2 Mass balance equations (superscript 0 indicates value in the influent)

$$V\frac{dS_S}{dt} = Q_O S_S^0 - Q_E S_S - Q_W S_S - \frac{1}{(1-k_{UAP}-k_{EPS})Y_H}p_1 V - \frac{1}{(1-k_{UAP}-k_{EPS})Y_H}p_3 V + p_9 V - p_{12} V - p_{14} V$$

$$V\frac{dX_S}{dt} = Q_O X_S^0 - Q_W X_S + (1-f_P)p_6 V + (1-f_P)p_7 V - p_9 V$$

$$V\frac{dX_{BH}}{dt} = Q_O X_{BH}^0 - Q_W X_{BH} + p_1 V + p_2 V + p_3 V + p_4 V - p_6 V$$

$$V\frac{dX_{BA}}{dt} = Q_O X_{BA}^0 - Q_W X_{BA} + p_5 V - p_7 V$$

$$V\frac{dX_P}{dt} = Q_O Q_P^0 - Q_W X_P + f_P p_6 V + f_P p_7 V$$

$$V\frac{dS_{UAP}}{dt} = Q_O S_{UAP}^0 - Q_E S_{UAP} - Q_W S_{UAP} - \frac{1}{Y_{SMP}}p_2 V - \frac{1}{Y_{SMP}}p_4 V + k_{UAP}p_{14} V + k_{UAPa}p_{15} V$$

$$V\frac{dS_{BAP}}{dt} = Q_O S_{BAP}^0 - Q_E S_{BAP} - Q_W S_{BAP} - \frac{1}{Y_{SMP}}p_2 V - \frac{1}{Y_{SMP}}p_4 V + p_{11} V$$

$$V\frac{dX_{EPS}}{dt} = Q_O X_{EPS}^0 - Q_W X_{EPS} - p_{11} V + p_{12} V + p_{13} V$$

$$V\frac{dS_O}{dt} = Q_O S_O^0 - Q_E S_O - Q_W S_O - \frac{1-(1-k_{UAP}-k_{EPS})Y_H}{(1-k_{UAP}-k_{EPS})Y_H}p_1 V - \frac{1-Y_{SMP}}{Y_{SMP}}p_2 V - \frac{4.57-Y_A}{Y_A}p_5 V + k_{LA}(S_{OS}-S_O)$$

$$V\frac{dS_{NO}}{dt} = Q_O S_{NO}^0 - Q_E S_{NO} - Q_W S_{NO} - \frac{1-(1-k_{UAP}-k_{EPS})Y_H}{2.86(1-k_{UAP}-k_{EPS})Y_H}p_3 V - \frac{1-Y_{SMP}}{2.86Y_{SMP}}p_4 V + \frac{1}{Y_A}p_5 V$$

$$V\frac{dS_{NH}}{dt} = Q_O S_{NH}^0 - Q_E S_{NH} - Q_W S_{NH} - i_{XB}p_1 V - i_{XB}p_2 V - i_{XB}p_3 V - i_{XB}p_4 V - \left(i_{XB}+\frac{1}{Y_A}\right)p_5 V + p_8 V - p_{13} V - p_{15} V$$

$$V\frac{dS_{ND}}{dt} = Q_O S_{ND}^0 - Q_E S_{ND} - Q_W S_{ND} - p_8 V + p_{10} V$$

$$V\frac{dX_{ND}}{dt} = Q_O X_{ND}^0 - Q_W X_{ND} + (i_{XB}-f_P i_{XP})p_6 V + (i_{XB}-f_P i_{XP})p_7 V - p_{10} V$$

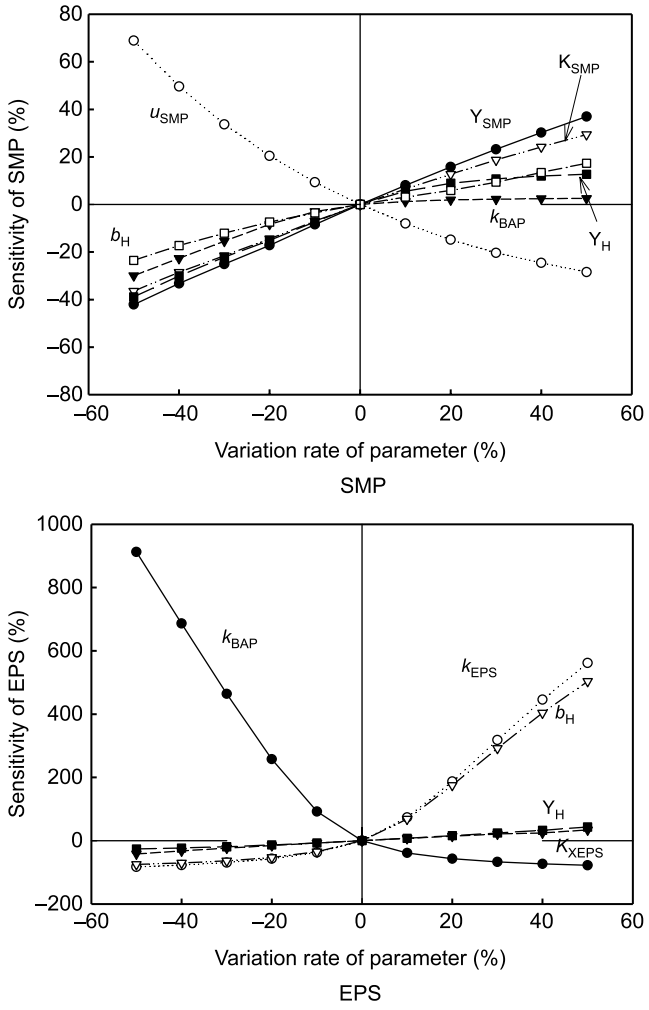

Figure 4 Sensitivity of selected parameters

However, the parameters directly related to the EPS and SMP formation were almost impossible to measure. Therefore, in this study, the yield coefficient (Y_H), growth rate (μ_H) and decay rate (b_H) were estimated since they were respected to be important because the SMP and EPS associated with growth and decay of microorganisms according to the unified model (Figure 3).

Kinetic parameters of MBRs

As shown in Table 3, it was found that MBR sludge had different microbial kinetic values as compared with the activated sludge process. In case of heterotrophic biomass, yield and growth rate of MBR sludge were smaller than activated sludge. On the contrary, the decay rate of MBR sludge was larger than activated sludge. However, in case of autotrophic biomass, yield and decay rate of MBR sludge were larger but growth rate was smaller than activated sludge.

Yield, growth rate, and decay rate were dependent on the SRT among the various microbial kinetic parameters of MBR. In heterotrophs, yield and growth rate decreased from 0.56 to 0.43 and from 3.25 day^{-1} to 1.17 day^{-1} with increasing SRT. But, decay rate increased from 0.60 day^{-1} to 0.77 day^{-1}. In autotrophs, yield and decay rate

Table 3 Comparison of kinetic parameter between MBR and CAS sludge (SRT 90 days)

	Autotrophs		Heterotrophs	
	MBR	CAS	MBR	CAS
Yield	0.30	0.24	0.43	0.67
Growth rate (day^{-1})	0.48	0.80	1.17	6.00
Decay rate (day^{-1})	0.18	0.08	0.77	0.62

increased from 0.25 to 0.30 and from 0.12 day^{-1} to 0.18 day^{-1} with increasing SRT. On the contrary, growth rate decreased from 0.67 day^{-1} to 0.48 day^{-1}.

Simulation of EPS and SMP concentration

Simulations calibrated with estimated parameters showed accurate results for SMP and EPS concentrations at various SRTs as shown in Figure 5. It suggested that the unified theory and its calibration with three parameters could be used for the simulating mechanisms of SMP and EPS.

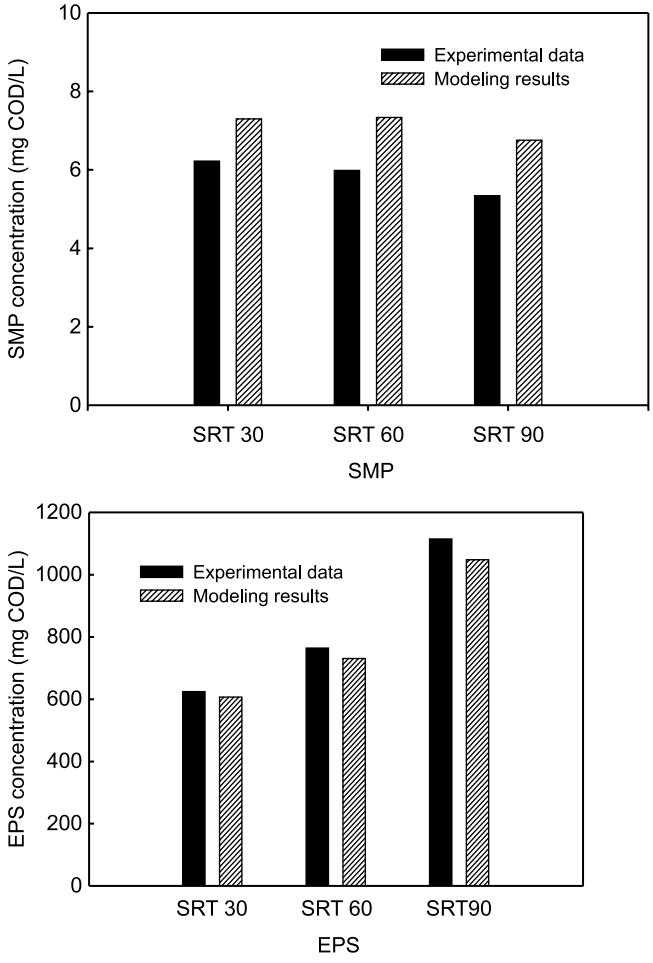

Figure 5 EPS and SMP concentration in the MBRs at various SRTs

Conclusions

MBR sludge, both of heterotrophs and autotrophs, showed different yield, growth rate and decay rate from activated sludge. Compared to the CAS sludge, MBR sludge showed a higher yield value (0.30) and decay rate (0.18 day^{-1}) of autotrophs. With the obtained kinetic constant and newly developed model, relatively accurate modeling of EPS and SMP in bioreactor was possible. In this model, the effect of SRT was not observed in SMP production but in EPS production, and the experimental results showed good agreements with the simulation results. Therefore, it is not recommended to use ASM1 kinetic parameters for the modeling of EPS and SMP production in MBR. With the unified EPS-SMP model, EPS and SMP production could be simulated so well that it could be applied for the membrane bio-fouling control.

References

APHA; AWWA; WPCF (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th edn, American Public Health Association, Washington.

Bai, R. and Leow, H.F. (2002). Microfiltration of activated sludge wastewater – the effect of system operation parameters. *Sep. Purif. Tech.*, **29**, 189–198.

Bura, R., Cheung, M., Liao, B., Finlayson, J., Lee, B.C., Droppo, I.G., Leppard, G.G. and Liss, S.N. (1998). Composition of extracellular polymeric substances in the activated sludge floc matrix. *Wat. Sci. Tech.*, **37**(4–5), 325–333.

Characklis, W.G. and Marshall, K.C. (1990). *Biofilms*, Wiley, New York.

Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A. and Smith, F. (1956). Colorimetric method for determination of sugars and related substances. *Analytical Chemist*, **28**(3), 265–275.

Frølund, B., Palmgren, R., Keiding, K. and Nielsen, P.H. (1996). Extraction of extracellular polymers from activated sludge using a cation exchange resin. *Wat. Res.*, **30**(8), 1749–1758.

Shin, H.-S. and Kang, S.-T. (2003). Characteristics and fates of soluble microbial products in ceramic membrane bioreactor at various sludge retention times. *Water Res.*, **37**(1), 121–127.

Nagaoka, H., Ueda, S. and Miya, A. (1996). Influence of bacterial extracellular polymers on the membrane separation activated sludge process. *Wat. Sci. Tech.*, **34**(9), 165–172.

Lowry, O.H., Rosebrough, N.J., Farr, A.L., and Randall, R.J. (1951). Protein measurement with the folin phenol reagent. *J. Biol. Chem*. **193**, 265–275.

Morgan, J.W., Forster, C.F. and Evison, L. (1990). A comparative study of the nature of biopolymers extracted from anaerobic and activated sludge. *Wat. Res.*, **24**(6), 743–750.

Rittmann, B.E. and McCarty, P.L. (2001). *Environmental Biotechnology: Principles and Applications*. Mc-Graw Hill, New York.

Vanrolleghem, P.A., Henri, S.H., Petersen, B., Ginestet, P. and Takacs, I. (1999). Estimating (combinitions of) activated sludge model No.1 parameters and components by respirometry. *Wat. Sci. Tech.*, **39**(1), 195–214.

Zeman, L.J. and Zydney, A.L. (1996). *Microfiltration and Ultrafiltration Principles and Application*. Marcel Dekker Inc, New York.