

A kinetic modeling for carbon metabolism in sequencing batch reactor under multiple aerobic/anoxic conditions

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Abstract In order to further investigate activated sludge system for better carbon metabolism and nitrogen removal with less energy consumption, a new kinetic model was established. The detailed description of the proposed model was introduced for understanding the mechanisms involved in the activated sludge system, especially simultaneous substrate storage and biomass growth (SSSG) processes and soluble microbial product generation. The evaluation of the proposed model was demonstrated by a lab-scale sequencing batch reactor (SBR) operated with three different sets, i.e., aeration/non-aeration (set 1), non-aeration/aeration/non-aeration (set 2), and alternating aeration/non-aeration (set 3) processes. The purpose was to investigate carbon metabolism under multiple aerobic/anoxic conditions. The calibrated results showed quite an acceptable model fit to the on-line measured dissolved oxygen (DO) data for the three SBR sets. Predictions of the calibrated model were successfully confirmed using off-line

analyses of soluble chemical oxygen demands (COD) and nitrogen dynamic variations, respectively. The simulated results showed that more SMP was generated under aerobic condition than that under anoxic condition, and more nitrate (S_{NO}) consumption resulted in less SMP generation, i.e., approximately 7% and 57% less extra carbon source in sets 2 and 3 were required to remove 8% and 58% of S_{NO} , respectively, compared with set 1. And the kinetics of SSSG process in the proposed model was indirectly validated by comparisons between experimental DO profiles and simulations. Therefore, the new model provides an effective technique for better optimizing the effluent COD and nitrogen with low energy cost in biological wastewater treatment plants.

Keywords Activated sludge modeling · SBR · Simultaneous substrate storage and biomass growth process (SSSG) · SMPs · Biological wastewater treatment

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Introduction

Activated sludge (AS) has been widely applied in wastewater treatment for carbon and nitrogen removals by carbon-based substrate consumption [i.e., chemical oxygen demand (COD)], nitrification, and denitrification processes. The truth that more substrate left for denitrification and less nitrite plus nitrate (S_{NO}) concentration will be expected in effluent has guided the designers to a multiple aerobic/anoxic or step-feed strategy for better nitrogen removal (Henze 1992; Nyberg et al. 1992; Chang and Hao 1996; Katsogiannis et al. 2003; Demuyne et al. 1994; Lin and Jing 2001; Larrea et al. 2001; Pulg et al. 2004; Guo et al. 2007; Pai et al. 2004; Zhu et al. 2009; Ge et al. 2010). While more substrate is consumed for denitrification and less dissolved oxygen (DO)

will be demanded for substrate degradation, therefore, less energy will be consumed (Tam et al. 1992; Demuyne et al. 1994; Chang and Ouyang 2000). As the energy crisis grows in future, it is necessary to further investigate activated sludge system for better carbon metabolism and nitrogen removal with less energy consumption.

As a helpful and powerful tool, mathematical modeling of AS systems has been widely applied to design, operate, or optimize the wastewater treatment process within limited time and financial budget (Henze et al. 2000). The increased comprehensive understanding of the reactions among the microorganisms and storage polymers to be an essential intermediate in the overall substrate removal in activated sludge systems led Activated Sludge Model no. 3 (ASM) to be proposed with first storage later growth based kinetics (Gujer et al. 1999). However, ASM3 failed to properly predict (a) the numerical discontinuity in the growth rate of biomass obtained in short-term respirometric batch experiments (Krishna and van Loosdrecht 1999), (b) large deviation of internal storage polymers (Krishna and van Loosdrecht 1999), (c) high rate of oxygen utilization in the feast phase and low rate in the famine phase (Karahangül et al. 2003) and, (d) effluent-soluble biodegradable organic matter (Lu et al. 2002; Oliveira-Esquerre et al. 2006). One main reason is that it assumed all readily biodegradable substrate to be first stored as internal storage polymers in the feast phase before being used for growth in the famine phase (Gujer et al. 1999). However, the mechanism of simultaneous storage and growth (SSSG) processes was confirmed more reasonable in the AS system under feast condition (Beccari et al. 2002; Benu et al. 2000; Carucci et al. 2001; Dircks et al. 2001; Krishna and van Loosdrecht 1999; Pratt et al. 2004; van Loosdrecht et al. 1997; Sin et al. 2005; Ni and Yu 2008).

The other reason is that ASM3 did not describe the mechanism of soluble microbial product (SMP) formation and degradation during substrate metabolism and endogenous respiration processes, which were divided into utilization-associated products (UAPs) and biomass-associated products (BAPs) (Rittmann et al. 1987; Barker and Stuckey 1999). The acknowledgment of the presence of SMP revolutionized the understanding of wastewater treatment systems. Previously, models of wastewater treatment systems including ASM3 have based on the Monod model which predicted that the effluent concentration of soluble biodegradable organic matters should be independent of influent substrate concentration. However, this did not agree with observations that increasing influent soluble COD (SCOD) would expect an increasing effluent SCOD. The incorporation of SMP formation and degradation paved the way for more accurate modeling of wastewater treatment (Barker and Stuckey 1999; Oliveira-Esquerre et al. 2006; Lu et al. 2002).

As the energy consumption of aeration is mainly used for substrate removal in biological wastewater treatment process, it is crucial and necessary to clearly simulate and predict carbon metabolism under aerobic and anoxic conditions. To this aim, a full kinetic model involving both SSSG and SMP mechanisms under aerobic and anoxic conditions is proposed in this paper. A lab-scale sequencing batch reactor (SBR) with multiple aeration cycles and single-feed strategy is employed to evaluate the proposed model.

Materials and methods

Experimental setup and operation

The experiments were performed using a lab-scale SBR with a valid volume of 11.0 L under room temperature ($22\pm 2^\circ\text{C}$). The SBR was a fill-and-draw system, in which wastewater was added during the fill period, simultaneously stirred and aerated during the aeration period, only stirred during non-aeration period. A part of the mixed liquor was withdrawn just before sedimentation period, and at the end of the cycle, the treated wastewater was decanted. A time controller was adopted to control the sequence program of SBR. The oxygen supply was not controlled so that additional information was available for calculation of the overall volumetric oxygen mass transfer coefficient $k_{\text{L}}a$ and the saturation oxygen concentration S_{O}^* .

Three kinds of SBR sets were conducted with a cycle of 8 h, i.e., 2 min for input, 7 h for reaction, 55 min for settlement, 2 min for drain, and last 1 min for idle period. The detailed operation conditions for each set are shown in Table 1. Set 1 was operated under aeration/non-aeration condition. The advantage of this process was that the feast and famine phase for biomass could be preformed in the same aerobic period which is convenient to investigate the SSSG process and SMP generation under aerobic conditions. The aeration cycle for set 2 was divided into non-aeration/aeration/non-aeration period. The purpose of set 2 was to investigate the SSSG process and SMP generation in feast phase under anoxic condition. Set 3 was conducted with multi-aeration/non-aeration in order to progress the feast and famine phase in both aerobic and anoxic conditions.

The sludge was taken from a local A/O wastewater treatment plant (WWTP) (Shanghai, China) which performed COD removal, nitrification, and denitrification. Synthetic municipal wastewater was prepared with glucose, sodium acetate, protein, and starch as carbon source, urea and ammonium chloride as nitrogen, and potassium dihydrogen phosphate as phosphorus sources, respectively, along with trace nutrients addition which contained (in

Table 1 SBR performances with different operation conditions

Parameters processes	Performance (aeration cycle)	K_{La} (day ⁻¹)	SRT (h)	Total aeration time (h)
Set 1	A/non (5.5/1.5) h	110	15	5.5
Set 2	Non/A/non (2/4/1) h	80	8	4
Set 3	A/non/A/non/A/non/A (1.5/0.5/1.5/0.5/1.5/0.5/1) h	100	34.7	5.5

A aeration, Non non-aeration, SRT sludge retention time

grams per cubic meter): H_3BO_4 , 0.22; $ZnSO_4 \cdot 7H_2O$, 0.21; $MnSO_4 \cdot H_2O$, 0.11; $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 0.13; $CoCl_2$, 0.22; $CuSO_4$, 0.07; and $NiSO_4 \cdot 6H_2O$, 0.34. The total COD, soluble COD, particulate COD, ammonia and ammonium nitrogen (S_{NH}), and pH of wastewater were 460 ± 20 g m⁻³, 260 ± 15 g m⁻³, 200 ± 20 g m⁻³, 24 ± 4 g N m⁻³, and 7.0 ± 0.1 , respectively.

Analytical procedures

SCOD, S_{NH} , nitrite, and nitrate (S_{NO}) were sampled every several minutes and off-line analyzed to obtain a series of dynamic variation during one SBR cycle. SCODs were measured after filtration with 0.45 μ m membrane filter (PVDF). Biological oxygen demand (BOD) test showed that the residual SCOD was much lower compared to total COD of the synthetic municipal wastewater (around 1%), and most of the residual soluble organic matters after BOD test could pass through the 1 K molecular weight (MW) cut-off ultrafiltration (UF) membrane into filtrate (results not shown). Therefore, about 80% of the residual SCOD was used in this study as S_I . Since all the effluent soluble COD was composed of SMP and S_I , but not residual initial soluble and readily biodegradable substrate (S_S) as it can be totally consumed during enough long reaction period (at least 1 h) in these experiments (see next section), SMP was

obtained from the difference between effluent SCOD and S_I . Then, effluent utilization-associated product (UAP) and biomass-associated product (BAP) were separated with different MW cut-off UF membranes in high pressure-stirred cells according to the different MW distribution of SMP (Logan and Wagenseller 2000).

Only total particulate organic matter in the influent was measured during the experiment. Inert particulate organic material X_I and slowly biodegradable substrate X_S were not directly determined, instead, the comparison of MLSS concentrations between the simulation and the measurements was used to calibrate the quantities of X_I and X_S .

Other analyses were performed following standard methods (APHA 1999). The detailed influent and effluent component values for each SBR sets are listed in Table 2.

Results

Model developments

Metabolism pathway and model mechanism

Activated sludge process is a complex biological system including many different functional microorganisms and

Table 2 The influent and effluent components measurements for three different SBR performances

Set components	Set 1		Set 2		Set 3	
	Input	Output	Input	Output	Input	Output
TCOD (mg/L)	470	–	465.6	–	460.4	–
SCOD (mg/L)	278	27.9	279.8	12.1	256.2	26.1
S_I (mg/L)	4.7	4.7	4.6	4.6	4.6	4.6
S_S (mg/L)	273.3	–	275.2	–	251.6	–
UAP (mg/L)	–	5.9	–	1.9	–	5.0
BAP (mg/L)	–	18.1	–	4.5	–	19.9
X_S (mg/L)	187.3	–	181.2	–	199.6	–
X_I (mg/L)	4.7	–	4.6	–	4.6	–
S_{NH} (mg N/L)	24.2	0.7	21.1	0.05	24.5	0.7
S_{NO} (mg N/L)	–	19.3	–	7.8	–	17.7
S_{ALK} (mol/L)	3.15	0.8	3.2	0.2	3.22	0.8
MLSS (mg/L)	1,341	–	1,055	–	1,881	–

All the concentrations in the table are average values for several measurements ($n \geq 3$)
 TCOD total chemical oxygen demand, UAP utilization-associated product, BAP biomass-associated product, MLSS mixed liquor suspended solids, SCOD soluble COD

related biological processes. The major known groups associated with the carbon metabolism in ASM3 are heterotrophic microorganisms including aerobic heterotrophic microorganisms, nitrite-reducing microorganisms, and nitrate-reducing microorganisms (Henze et al. 2000). However, being autotrophs, nitrifiers reduce inorganic carbon to form organic carbon during which SMP, i.e., UAP, is thought to be formed primarily through the portion of electron flow to cell synthesis (Furumai and Rittmann 1992), which means autotrophic microorganisms (including ammonium-oxidizing autotrophs and nitrite-oxidizing autotrophs) have inherent relation with the carbon metabolism. Hence, in this research, both heterotrophic microorganisms and autotrophic microorganisms are responsible for the carbon metabolism. According to the proposed model, the interaction relationships among these microorganisms for carbon metabolism pathway in activated sludge system were illustrated in Figs. 1 and 3 (Table 3).

Model kinetics for SSSG processes

The proposed model for describing the biodegradable substrate metabolism is very different from ASM3 where the initial substrate has been deemed to be first up-taken and stored by microorganisms during feast phase and further utilized for biological maintenance and growth during famine phase (Gujer et al. 1999). As most WWTPs are typically operated at high sludge retention time (SRT), substrate storage and direct growth on substrate were occurred simultaneously, and the storage became dominant under high SRT conditions, f_{STO} can be considered as a constant value when considering many influencing factors altogether (Sin et al. 2005). The constant value was often confirmed experimentally (Benu et al. 2000, 2002; Dircks et al. 2001). Consequently, the simultaneous storage and growth process have been described during the feast phase in this model (see Fig. 1). The kinetic expressions describing the growth on

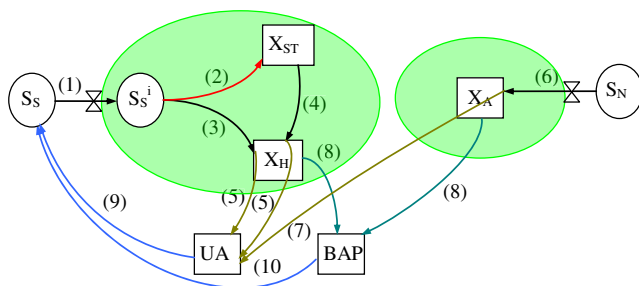


Fig. 1 Schematic of carbon flow among microorganisms for the proposed model: (1) uptake; (2) storage; (3) growth on S_S ; (4) growth on X_{STO} ; (5) UAP formation; (6) growth on S_{NH} ; (7) UAP formation; (8) BAP formation; (9) UAP hydrolysis; (10) BAP hydrolysis.

S_S under aerobic and anoxic conditions are defined in Eqs. 1 and 2, respectively.

$$r_{\text{growth},S} = \mu_{\text{MAX},S} \cdot (1 - f_{\text{STO},O}) \cdot \frac{S_O}{K_O + S_O} \cdot \frac{S_{\text{NH}}}{K_{\text{NH}} + S_{\text{NH}}} \cdot \frac{S_{\text{ALK}}}{K_{\text{ALK}} + S_{\text{ALK}}} \cdot \frac{S_S}{K_S + S_S} \cdot X_H \quad (1)$$

or

$$\eta_{\text{NO}} \cdot \mu_{\text{MAX},S} \cdot (1 - f_{\text{STO},\text{NO}}) \cdot \frac{K_O}{K_O + S_O} \cdot \frac{S_{\text{NO}}}{K_{\text{NO}} + S_{\text{NO}}} \cdot \frac{S_{\text{NH}}}{K_{\text{NH}} + S_{\text{NH}}} \cdot \frac{S_{\text{ALK}}}{K_{\text{ALK}} + S_{\text{ALK}}} \cdot \frac{S_S}{K_S + S_S} \cdot X_H \quad (2)$$

where $r_{\text{growth},S}$ represents the rate of direct growth on substrate; $f_{\text{STO},O}$ and $f_{\text{STO},\text{NO}}$ are the ratio constants of storage products to substrate uptake under aerobic and anoxic conditions, respectively. The other notations are taken from ASM3 terminologies (Gujer et al. 1999), while the kinetic expressions for storage under aerobic and anoxic conditions are defined in Eqs. 3 and 4, respectively, in which r_{STO} represents the rate of substrate storage.

$$r_{\text{STO}} = k_{\text{STO}} \cdot f_{\text{STO},O} \cdot \frac{S_O}{K_O + S_O} \cdot \frac{S_S}{K_S + S_S} \cdot X_H \quad (3)$$

or

$$\eta_{\text{NO}} \cdot k_{\text{STO}} \cdot f_{\text{STO},\text{NO}} \cdot \frac{K_O}{K_O + S_O} \cdot \frac{S_{\text{NO}}}{K_{\text{NO}} + S_{\text{NO}}} \cdot \frac{S_S}{K_S + S_S} \cdot X_H \quad (4)$$

However, it does not mean that during the feast phase, biomass cannot consume X_{STO} simultaneously, which means that there is no switch function $\frac{K_S}{K_S + S_S}$ to control internal storage products X_{STO} consumption. Therefore, the kinetic expressions describing the degradation of storage products (i.e., growth on X_{STO}) are defined in Eqs. 5, 6, and 7. Here, Sin et al. (2005) described the degradation of storage products and indicated the positive correlation between X_{STO} degradation rate and X_{STO} concentration.

$$r_{\text{growth},\text{STO}} = \mu_{\text{MAX},\text{STO}} \cdot \frac{S_O}{K_O + S_O} \cdot \frac{S_{\text{NH}}}{K_{\text{NH}} + S_{\text{NH}}} \cdot \frac{S_{\text{ALK}}}{K_{\text{ALK}} + S_{\text{ALK}}} \cdot \frac{(X_{\text{STO}}/X_H)^2}{K_2 + K_1 \cdot (X_{\text{STO}}/X_H)} \cdot X_H \quad (5)$$

or

$$\eta_{\text{NO}} \cdot \mu_{\text{MAX},\text{STO}} \cdot \frac{K_O}{K_O + S_O} \cdot \frac{S_{\text{NH}}}{K_{\text{NH}} + S_{\text{NH}}} \cdot \frac{S_{\text{ALK}}}{K_{\text{ALK}} + S_{\text{ALK}}} \cdot \frac{(X_{\text{STO}}/X_H)^2}{K_2 + K_1 \cdot (X_{\text{STO}}/X_H)} \cdot X_H \quad (6)$$

Table 3 The proposed model matrix: simplified stoichiometric and component matrix

Processes	S_O O ₂	S_I COD	S_S COD	UAP COD	BAP COD	S_{NH} N	S_{NO} N	X_I COD	X_H COD	X_{STO} COD	X_A COD	Equations
1.1 Hydrolysis of UAP		f_{S_I}	$1-f_{S_I}$	-1		$f_{NH}^{UAP} f_{S_I} f_{S_I} (1-f_{S_I}) f_{N,S_S}$						16
1.2 Hydrolysis of BAP			f_{S_I}		-1	$f_{NH}^{BAP} f_{S_I} f_{S_I} (1-f_{S_I}) f_{N,S_S}$						17
2.1 Aerobic storage of S_S	$-1+Y_{STO,O}$		-1			$f_{NH}^{S_S}$	$(-1+Y_{STO,NO})/2.86$			$Y_{STO,O}$		3
2.2 Anoxic storage of S_S			-1			$f_{NH}^{S_S}$				$Y_{STO,NO}$		4
3.1 Aerobic growth on S_S	$1+k_{UAP,O} - \frac{1}{Y_{I,O}}$		$\frac{-1}{Y_{I,O}}$	$k_{UAP,O}$		$-f_{NH}^{BM} - \frac{f_{NH}^{UAP} k_{UAP,O} - f_{NH}^{SS}}{Y_{I,O}}$		1				1
3.2 Anoxic growth on S_S			$\frac{-1}{Y_{I,NO}}$	$k_{UAP,NO}$		$-f_{NH}^{BM} - \frac{f_{NH}^{UAP} k_{UAP,NO} - f_{NH}^{SS}}{Y_{I,NO}}$	$\frac{1+k_{UAP,O}}{2.86} - \frac{1}{2.86 Y_{I,O}}$	1				2
4.1 Aerobic growth on X_{STO}	$1 - \frac{1}{Y_{2,O}} + k_{USTO,O}$			$k_{UST,O}$		$f_{NH}^{BM} - k_{USTO,O} f_{N,UAP} Y_{2,O}$		1		$\frac{-1}{Y_{2,O}}$		5
4.2 Anoxic growth on X_{STO}				$k_{UST,NO}$		$-f_{NH}^{BM} - \frac{k_{USTO,NO} f_{NH}^{UAP}}{Y_{2,NO}}$	$\frac{1+k_{USTO,NO}}{2.86} - \frac{1}{2.86 Y_{2,NO}}$	1		$\frac{-1}{Y_{2,NO}}$		6
5.1 Aerobic endogenous respiration of X_H	$-1+k_{BAP,O} + f_{-1}$				$k_{BAP,O}$	$f_{NH}^{BM} - k_{BAP,O} f_{N,BAP} - f_{NH}^{XI}$		f_i	-1			9
5.2 Anoxic endogenous respiration of X_H					$k_{BAP,NO}$	$f_{NH}^{BM} - k_{BAP,NO} f_{N,BAP} - f_{NH}^{XI}$	$(-1+k_{BAP,O} + f_i)/2.86$	f_i	-1			10
6. Nitrification	$1+k_{UAPA} + \frac{1}{Y_A}$			k_{UAPA}		$-f_{NH}^{BM} - \frac{1+f_{NH}^{UAP} k_{UAPA}}{Y_A}$	$\frac{1}{Y_A}$			1		15
7. Aerobic endogenous respiration of X_A	$k_{BAPA,O} + f_{-1}^{-1} k_B$				$k_{BAPA,O}$	$f_{NH}^{BM} - k_{BAPA,O} f_{N,BAP} - f_{NH}^{XI}$		f_i		-1		11
8. Anoxic endogenous respiration of X_A					k_{BAPANO}	$f_{NH}^{BM} - k_{BAPANO} f_{N,BAPA} - k_{N,BAPANO}$	$(k_{N,BAPANO} + f_i - 1)/2.86$	f_i		-1		12
1. COD	-1	1	1	1	1		-4.57		1	1		
2. Nitrogen		f_{N,S_I}	f_{N,S_S}	$f_{N,UAP}$	$f_{N,BAP}$	1		f_{N,X_I}	$f_{N,BM}$			$f_{N,BM}$

Other parts not showed in this new model matrix are as the same as the original ASM3
 UAP utilization-associated product, BAP biomass-associated product, COD chemical oxygen demand

$$f(X_{\text{STO}}/X_{\text{H}}) = \frac{(X_{\text{STO}}/X_{\text{H}})^2}{K_2 + K_1(X_{\text{STO}}/X_{\text{H}})} \quad (7)$$

where $r_{\text{growth, STO}}$ is the rate of biomass growth on X_{STO} ; K_1 is the regulation constant of biomass as a function of $X_{\text{STO}}/X_{\text{H}}$ and $K_2 = K_{\text{STO}} \cdot K_1$. Under the famine condition, readily soluble biodegradable substrates have been exhausted and internal storage products X_{STO} are as the main energy source (Eqs. 5 and 6). The relationship is described as Eq. 7.

Model kinetics for SMP formation and degradation

Since UAP and BAP origin from microbial but not the residual influent substrate, the formation and degradation of SMP should be included into the new activated sludge model. SMP can be generated through the whole processes of substrate metabolism, biomass growth, and even endogenous metabolism. In this model, the only source of BAP is from endogenous respiration metabolism of heterotrophic and autotrophic microorganisms (i.e., X_{H} and X_{A}), where the formation rates ($r_{\text{BAP, formation}}$) are proportional to the concentration of related biomass. The kinetic expression of describing BAP formation process is shown in Eq. 8.

$$r_{\text{BAP, formation}} = k_{\text{BAP}} \cdot r_{X_{\text{H}}, \text{ deg}} + k_{\text{BAPA}} \cdot r_{X_{\text{A}}, \text{ deg}} \quad (8)$$

$$r_{X_{\text{H}}, \text{ deg}} = b_{\text{H,O}} \frac{S_{\text{O}}}{K_{\text{O}} + S_{\text{O}}} X_{\text{H}} \quad (9)$$

or

$$b_{\text{H,NO}} \frac{K_{\text{O}}}{K_{\text{O}} + S_{\text{O}}} \cdot \frac{S_{\text{NO}}}{K_{\text{NO}} + S_{\text{NO}}} X_{\text{H}} \quad (10)$$

$$r_{X_{\text{A}}, \text{ deg}} = b_{\text{A,O}} \frac{S_{\text{O}}}{K_{\text{A,O}} + S_{\text{O}}} X_{\text{A}} \quad (11)$$

or

$$b_{\text{A,NO}} \frac{K_{\text{A,O}}}{K_{\text{A,O}} + S_{\text{O}}} \cdot \frac{S_{\text{NO}}}{K_{\text{A,NO}} + S_{\text{NO}}} X_{\text{A}} \quad (12)$$

where, $r_{X_{\text{H}}, \text{ deg}}$ is the endogenous respiration rate of heterotrophic microorganisms (Eqs. 9 and 10 for aerobic and anoxic conditions, respectively); $r_{X_{\text{A}}, \text{ deg}}$ is the endogenous respiration rate of autotrophic microorganisms (Eqs. 11 and 12); and k_{BAP} and k_{BAPA} represent BAP formation rate constants.

Compared to BAP formation, the generation of UAP is more complicated. One part of UAP is produced in

proportion to the rate of heterotrophic microorganisms' direct growth on substrate under the feast phase, storage product degradation for heterotrophic microorganisms' growth under feast and famine conditions, and autotrophic microorganisms' growth process, respectively. The kinetic expression of describing UAP formation process is shown in Eqs. 13 and 14.

$$r_{\text{UAP, formation}} = k_{\text{UAP,O}} \cdot r_{\text{growth, Ss}} + k_{\text{USTO,O}} \cdot r_{\text{growth, STO}} + k_{\text{UAPA}} \cdot r_{\text{growth, XA}} \quad (13)$$

or

$$k_{\text{UAP,NO}} \cdot r_{\text{growth, Ss}} + k_{\text{USTO,NO}} \cdot r_{\text{growth, STO}} \quad (14)$$

$$r_{\text{growth, XA}} = \mu_{\text{A}} \frac{S_{\text{O}}}{K_{\text{A,O}} + S_{\text{O}}} \cdot \frac{S_{\text{NH}}}{K_{\text{A,NH}} + S_{\text{NH}}} \cdot \frac{S_{\text{ALK}}}{K_{\text{A,ALK}} + S_{\text{ALK}}} X_{\text{A}} \quad (15)$$

where k_{UAP} , k_{USTO} , and k_{UAPA} represent UAP formation rate constants, $r_{\text{growth, XA}}$ is the growth rate of autotrophic microorganisms, and μ_{A} is autotrophic maximum growth rate (Eq. 15).

The generated SMP can also be biodegradable. Some studies even assumed that biomass can grow on BAP directly which can be described as a Monod-type reaction (Rittmann et al. 1987; Orhon et al. 1989; Boero et al. 1991; Furumai and Rittmann 1992; Lapidou and Rittmann 2002). However, Jiang et al. (2008) indicated SMP had a larger molecular weight that may not directly pass through the cell membrane, which means that the SMP should first be hydrolyzed into small readily biodegradable substrate. They also proposed a simple first-order kinetic relation with respect to SMP and biomass concentration to simplify the model. The relationships are described as Eqs. 16 and 17.

Hydrolysis of SMP with first-order kinetic expressions is as follows:

$$r_{\text{UAP, deg}} = k_{\text{H,UAP}} \cdot \text{UAP} \cdot X_{\text{H}} \quad (16)$$

$$r_{\text{BAP, deg}} = k_{\text{H,BAP}} \cdot \text{BAP} \cdot X_{\text{H}} \quad (17)$$

where $r_{\text{UAP, degradation}}$ and $r_{\text{BAP, degradation}}$ represent UAP and BAP degradation rate and $k_{\text{H, UAP}}$ and $k_{\text{H, BAP}}$ are the hydrolysis rate constants. From a model applicable point of view, using the hydrolysis of SMP instead of direct SMP degradation in Monod form is reasonable and most of important, since less parameters were introduced in SMP degradation mechanism (Jiang et al. 2008). Hence, this mechanism is also introduced into this new model.

Experimental results

The lab-scale SBR system for each performance was operated with the same influent characteristics for at least 40 days. The system was considered to have reached a steady-state condition when the effluent qualities including COD, $\text{NH}_4^+\text{-N}$, and $\text{NO}_x^-\text{-N}$ were maintained nearly the same after successive 7 days of monitoring. The summarized steady-state influent and effluent SCOD, S_{NH} , S_{NO} , and SMP (UAP and BAP, respectively) measurements for three different SBR performances are listed in Table 2. And the experimental results of DO, soluble COD, and S_{NH} and S_{NO} variations during 1 cycle for each SBR performance are shown in Figs. 2 and 4, respectively. As it is known that oxygen consumption mainly comes from three demands, i.e., substrate utilization, S_{NH} oxidation, and biomass endogenous respiration, and oxygen is always demanded for biomass endogenous respiration throughout the whole activated sludge process; therefore, a brief explanation with corresponding SCOD and S_{NH} variations in Figs. 2b, 3b, and 4b would reasonably interpret the DO variations in Figs. 2a, 3a, and 4a, respectively. However, as can be seen in Fig. 2a, as the DO value reduced to 0 after aeration pause, S_{NO} concentration should decrease obviously at around the 6.5th h due to denitrification. In contrast, the final S_{NO} curve did not decrease, which will be discussed later.

Compared with set 1 performance, DO concentration in Fig. 3a did not reduce to 0 in an hour after last aeration pause. Since the corresponding experimental measurements in Fig. 3b could not clearly interpret this phenomenon, a further explanation would be demonstrated in the next section after simulations.

Parameter determination and simulation strategy

The procedure for parameter calibration is very important, since appropriate parameters for wastewater characteristic can improve the accuracy of simulation. However, this does not mean that it is necessary to evaluate these parameters on a case by case basis. The actual values used are not critical as long as they are of the appropriate order of magnitude and are small in comparison with operation condition. This suggests that slightly changed default values derived from literatures would be satisfactory (Henze et al. 2000). Therefore, the model calibration procedure used in this study was a process of adjusting model parameter values to closely agree with the measured data

The initial parameter values used in this research were firstly derived from the literature (Fan et al. 2009; Jiang et al. 2008; de Silva and Rittmann 2000; Furumai and Rittmann 1992; Gujer et al. 1999) or estimation or

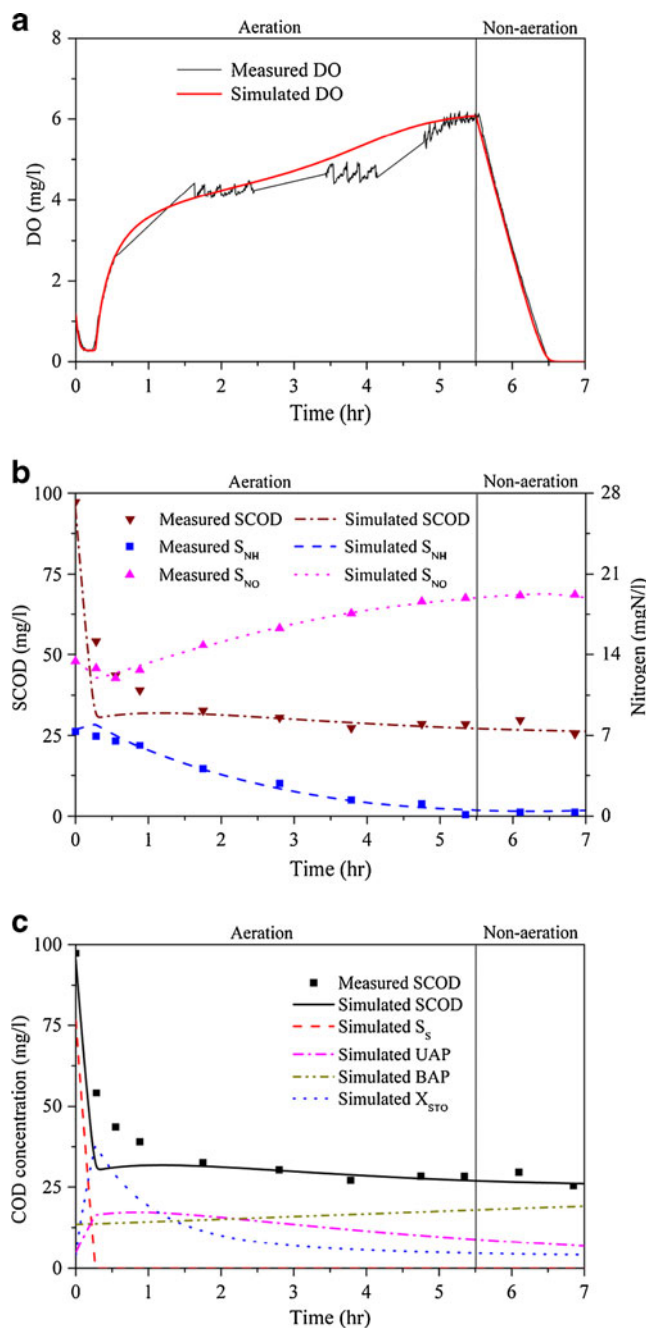


Fig. 2 Simulations of set 1 process (a) model calibration with measured DO, R is 0.991. (b) Comparisons of COD and nitrogen variations during one SBR cycle between ASMP model and experimental measurements, R of SCOD, S_{NH} , and S_{NO} are 0.939, 0.992, and 0.993, respectively. (c) Supplement simulation for predictions of carbon-based substrate metabolism: SCOD, S_s , UAP, BAP, and X_{sto}

measurement (see Table 4), and the global parameter sensitivity analysis with the Monte Carlo Estimation of the Sobol’ Sensitivity Indices was carried out to distinguish the sensitive parameters (Sobol 1993). These identified parameters associated with effluent SCOD, i.e., k_{UAP} , k_{STOU} , k_{USTO} , k_{BAP} , and k_{STOB} , with oxygen consumption,

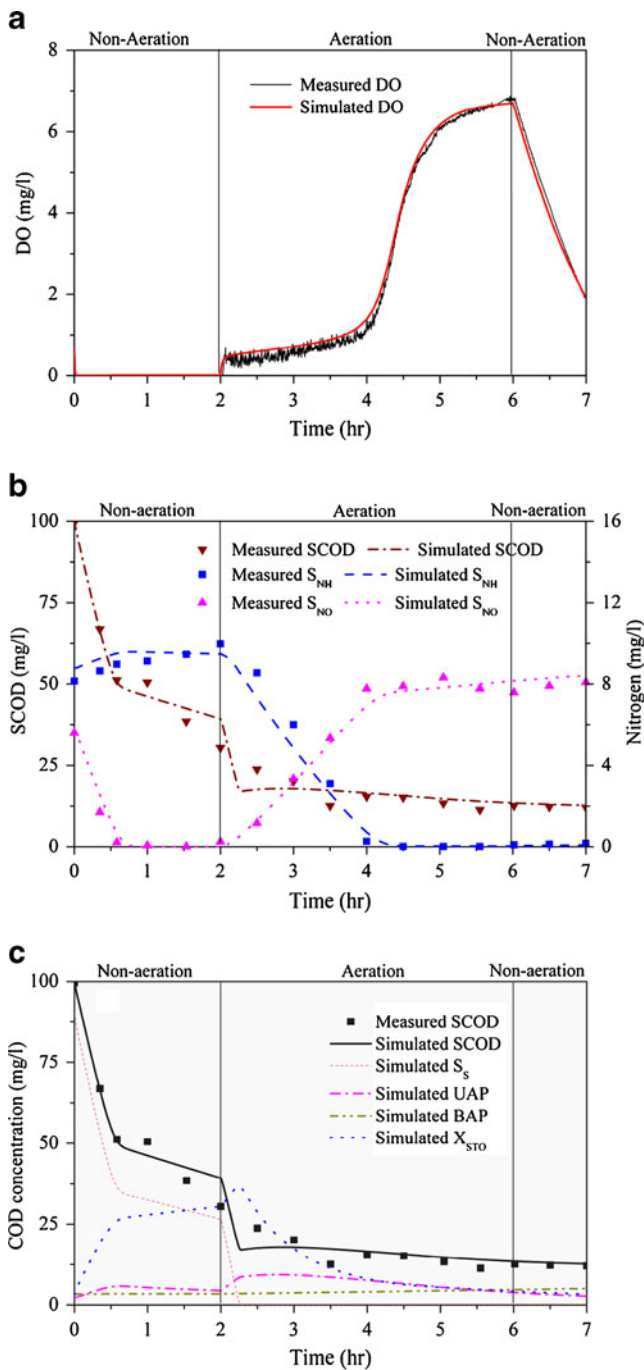


Fig. 3 Simulations of set 2 process (a) model calibration with measured DO, R is 0.995. (b) Comparisons of COD and nitrogen variations during one SBR cycle between ASMP model and experimental measurements; R of SCOD, S_{NH} , and S_{NO} are 0.990, 0.993, and 0.989, respectively. (c) Supplement simulation for predictions of carbon-based substrate metabolism: SCOD, S_s , UAP, BAP, and X_{STO}

i.e., μ_A , $\mu_{MAX, S}$, $\mu_{MAX, STO}$, f_{STO} , k_{STO} , k_{STOU} , and k_{STOB} , and with nitrogen metabolisms, i.e., $K_{A, NH}$ and K_{NO} , were calibrated, respectively, based on the measured data in a lab-scale test with the calibration procedure as described in references (Vanrolleghem et al. 2003; Hulsbeek et al. 2002;

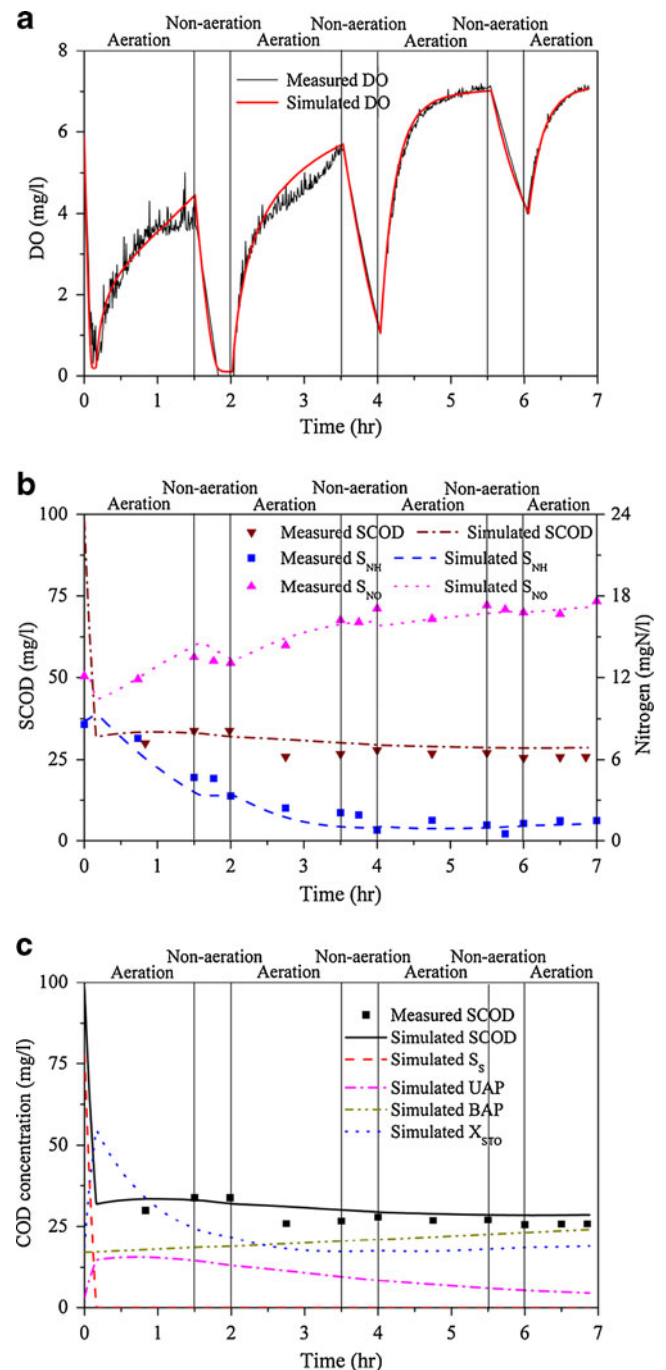


Fig. 4 Simulations of set 3 process (a) model calibration with measured DO, R is 0.995. (b) Comparisons of COD and nitrogen variations during one SBR cycle between ASMP model and experimental measurements, R of SCOD, S_{NH} , and S_{NO} are 0.996, 0.972, and 0.971, respectively. (c) Supplement simulation for predictions of carbon-based substrate metabolism: SCOD, S_s , UAP, BAP, and X_{STO}

Corominas et al. 2011). Finally, the parameter recalibrations were conducted just after the evaluations. As it is known that a process with different operation parameters and same influent could affect the effluent water quality, it is

Table 4 Kinetic and stoichiometric coefficients for the optimal calibration of experimental data (20°C)

Parameter	Definitions	Values	Source	Parameter	Definitions	Values	Source
b_A, NO	Anoxic endogenous respiration rate (day^{-1})	0.07 ± 0.004	Estimated	$k_{BAPA, NO}$	BAP anoxic formation constant (-)	0.1	de silva and Rittmann 2000
b_A, O	Endogenous decay rate coefficient of X_{STO} (day^{-1})	0.26 ± 0.005	Estimated	$k_{HI, BAP}$	BAP maximum hydrolysis rate ($g^{-1} day^{-1}$)	7.41×10^{-7}	Jiang et al. 2008
$b_{HI, NO}$	Anoxic endogenous respiration rate (day^{-1})	0.13 ± 0.006	Estimated	$k_{HI, UAP}$	UAP maximum hydrolysis rate ($g^{-1} day^{-1}$)	0.0102	Jiang et al. 2008
$b_{HI, O}$	Biomass endogenous decay rate coefficient (day^{-1})	0.25 ± 0.006	Estimated	K_{NH}	Ammonium saturation constant ($g N m^{-3}$)	0.01	Henze et al. 2000
f_I	Fraction of X_I in decay (-)	0.2	Henze et al. 2000	K_{NO}	Saturation constant ($g N m^{-3}$)	0.5	Henze et al. 2000
f_{SI}	Fraction of S_I in hydrolysis (-)	0	Henze et al. 2000	K_O	DO affinity constant ($g O_2 m^{-3}$)	0.2	Estimated
$f_{STO, NO}$	Fraction of substrate used for anoxic storage (-)	0.5	Estimated	K_S	Substrate affinity constant ($g COD m^{-3}$)	0.7	Sin et al. 2005
$f_{STO, O}$	Fraction of substrate used for aerobic storage (-)	0.68	Estimated	$k_{STO, O}$	Maximum storage rate (day^{-1})	12.7 ± 0.7	Estimated
$i_{N, BAP}$	N content of BAP ($g N g^{-1} COD$)	0.02	Estimated	$k_{UAP, NO}$	UAP anoxic formation constant (-)	0.2	Estimated
$i_{N, BM}$	N content of biomass, X_{HI}, X_A ($g N g^{-1} COD$)	0.05	Henze et al. 2000	$k_{UAP, O}$	UAP aerobic formation constant (-)	0.2	Estimated
$i_{N, SI}$	N content of S_I ($g N g^{-1} COD$)	0.01	Estimated	k_{UAPA}	UAP formation constant (-)	0.1	Estimated
$i_{N, SS}$	N content of S_S ($g N g^{-1} COD$)	0.02	Measured	$k_{USTO, NO}$	UAP anoxic formation constant (-)	0.2	Estimated
$i_{N, UAP}$	N content of UAP ($g N g^{-1} COD$)	0.03	Estimated	$k_{USTO, O}$	UAP aerobic formation constant (-)	0.2	Estimated
$i_{N, XI}$	N content of X_I ($g N g^{-1} COD$)	0.03	Estimated	Y_1, NO	Anoxic yield coefficient (-)	0.59	Sin et al. 2005
$i_{N, XS}$	N content of X_S ($g N g^{-1} COD$)	0.02	Measured	Y_1, O	Aerobic yield coefficient (-)	0.67	Sin et al. 2005
K_1	Biomass controlling degradation rate of X_{STO} constant (-)	0.102	Estimated	Y_2, NO	Anoxic yield coefficient (-)	0.54	Sin et al. 2005
K_2	The affinity of biomass to biomass storage fraction (-)	0.0012	Estimated	Y_2, O	Aerobic yield coefficient (-)	0.63	Sin et al. 2005
$K_{A, ALK}$	Bicarbonate saturation constant ($mmol l^{-1}$)	0.5	Henze et al. 2000	Y_A	Yield coefficient (-)	0.24	Henze et al. 2000
$K_{A, NH}$	Ammonium saturation ($g N m^{-3}$)	1.0	Henze et al. 2000	$Y_{STO, NO}$	Anoxic yield coefficient (-)	0.8	Sin et al. 2005
$K_{A, NO}$	Saturation constant ($g N m^{-3}$)	0.5	Henze et al. 2000	$Y_{STO, O}$	Aerobic yield coefficient (-)	0.85	Sin et al. 2005
$K_{A, O}$	Oxygen saturation ($g O_2 m^{-3}$)	0.5	Henze et al. 2000	η_{NO}	Anoxic reduction factor	0.6	Henze et al. 2000
K_{ALK}	Bicarbonate saturation constant ($mmol l^{-1}$)	0.1	Henze et al. 2000	μ_A	Maximum growth rate (day^{-1})	1.6 ± 0.4	Estimated
$k_{BAP, NO}$	BAP anoxic formation constant (-)	0.1	de silva and Rittmann 2000	$\mu_{MAX, S}$	Maximum growth rate (day^{-1})	9.5 ± 0.5	Estimated
$k_{BAP, O}$	BAP aerobic formation constant (-)	0.1	de silva and Rittmann 2000	$\mu_{MAX, STO}$	Maximum growth rate (day^{-1})	2.5 ± 0.3	Estimated
$k_{BAPA, O}$	BAP aerobic formation constant (-)	0.1	de silva and Rittmann 2000				

Table 4 contains the different parts between ASM3 and the proposed model, in which other parameters can be obtained from ASM3 (Henze et al. 2000). The variations of parameters in the table were due to the temperature

UAP utilization-associated product, BAP biomass-associated product, COD chemical oxygen demand

therefore reasonable to take into consideration that the parameters were well validated after recalibrations. The measured DO data and the best fits of predictions were shown in Figs. 2a, 3a, and 4a. Since the correlation coefficients (R) for each DO were 0.991, 0.995, and 0.995, respectively, the simulated results of DO showed the model fits were quite acceptable, although there were a little difference in Fig. 2a from 3.5 to 4.5 h and in Fig. 4a from 2.5 to 3.5 h. The reason for these errors could be due to the air bubbles or sludge trapped near the surface of DO sensor, reducing the data record. The simulations of SCOD (R for each SBR process were 0.939, 0.990, and 0.996), S_{NH} (R for each SBR process were 0.992, 0.993, and 0.972), and S_{NO} (R for each SBR process were 0.993, 0.989, and 0.971) also demonstrated the good model fits as shown in Figs. 2b and 4b.

SBR system modeling, simulation, and parameter sensitivity analysis for each model were coded using MATLAB 7.0 (The MathWorks, Natick, MA). The differential equations were solved with its Runge–Kutta (ode45 or ode15s) equation. SBR model just contained aeration, non-aeration, and settlement modules. In simulation, it was hypothesized that there was no reaction during input and output periods due to the short time span in order to simplify the process calculation. The sedimentation of sludge in SBR process was observed under good condition due to the good sludge settling performance (negligible denitrification), and therefore, the biochemical reaction was also neglected in this period. Hence, under this condition, one-dimensional sedimentation model proposed by Takacs et al. (1991) was adopted as the module for sedimentation process of SBR system.

Discussion

Simulations for carbon-based substrates metabolism

In order to describe carbon-based substrate metabolism (S_S , UAP, BAP, and X_{STO} , respectively) during one SBR cycle, the supplemental simulations of each COD components in each sets were illustrated in Figs. 2c, 3c, and 4c in detail. It was found that under aerobic condition (Figs. 2c and 4c) S_S was exhausted rapidly within less than 0.5 h corresponding to DO sharp consumptions from the beginning to 0.5 h in Figs. 2a and 4a, respectively. Meanwhile, UAP and X_{STO} increased rapidly during S_S consumption, respectively. Thereafter, X_{STO} was the main substrate for biomass growth and maintenance, during which UAP was generated again. Then, UAP decreased gradually along with the steady increase of BAP as the reaction time went on, indicating a further biodegradability of UAP compared to BAP (Noguera et al. 1994; Rittmann and McCarty 2001). The simulated SMP variations could be indirectly demonstrated

by the measured SCOD variation curves after 0.3 h in Fig. 4c. The failure of measured SCOD data in Fig. 2c could be probably due to the measurement error.

However, under anoxic condition (Fig. 3c), the degradation of S_S was more complicated, i.e., a rapid consumption in 0.8 h followed a slight decline in next 1.2 h and finally a fast decrease to zero in 0.1 h after aeration. This phenomenon could be well interpreted by the DO and S_{NO} consumption in subpanels a and b of Fig. 3, respectively. It should be noted that from 0.8 to 2.0 h, since no DO and S_{NO} were left in the reactor as the subpanels a and b of Fig. 3 has shown, respectively, the SCOD consumption was probably contributed to mechanical agitation for mixing sludge that caused oxygen transfer from air phase into liquid. Meanwhile, UAP and X_{STO} also underwent a fast increase followed a gentle increase, and finally, a rapid increase during S_S consumption (Fig. 3c). Thereafter, UAP increased rapidly due to X_{STO} consumption and then it decreased gradually along with the steady increase of BAP in the reactor as the reaction time went on, which also indicated a further biodegradability of UAP compared to BAP (Noguera et al. 1994; Rittmann and McCarty 2001).

According to above discussion, it can be deduced that there should be a minimum SMP value (UAP plus BAP), after that point, SMP concentration would increase again which was more consistent with the practical performance of wastewater treatment plants (Barker and Stuckey 1999). Hence, a short reaction time or hydraulic retention time of SBR systems for municipal wastewater treatment is suggested in order to optimize effluent COD. The detailed time span would be easily obtained after using the proposed model in estimation and optimization of activated sludge systems.

SBR sets effect on substrate metabolism and SMP generation

As described in Table 1, set 1 and set 3 had the same span of aeration time, very close k_{LA} value and different SRT.

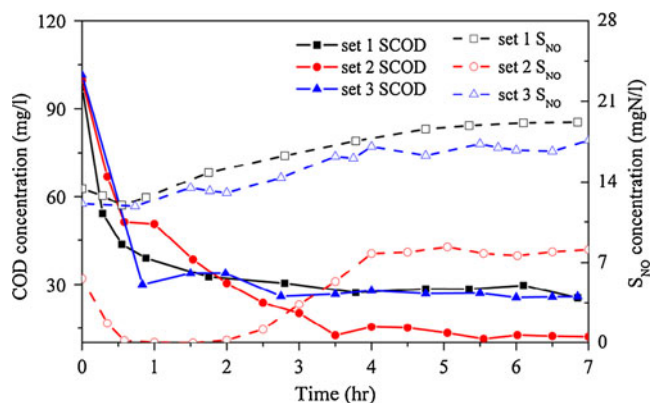


Fig. 5 Comparisons of SCOD and S_{NO} variations during one SBR cycle among the multiple aeration cycles

Since the simulation results indicated that the effect of k_L a variation from 100 to 110 day^{-1} on SMP generation could be ignored (results not shown), set 3 should have more SCOD according to literature which indicated longer SRT would generate more SMP (Barker and Stuckey 1999). However, the experimental measurements did not agree with the above conclusion (Table 2 and Fig. 5). On the contrary, the effluent SCOD and S_{NO} concentrations were approximately 7% and 8% lower in set 3 than that in set 1, respectively. In other words, 7% less extra carbon source was required to remove the residual S_{NO} , i.e., for 8% of N-removal. This result was confirmed by other investigation, in which 50% more extra carbon source was needed for traditional SBR cycle to remove the residual S_{NO} , compared with SBR system under multiple aeration cycle (short time span for each) and same SRT (Demuynck et al. 1994). Therefore, the reason for this phenomenon was due to the process operation conditions, i.e., aeration cycle pattern. As UAP formation rate under aerobic condition is larger than that under anoxic condition, less UAP was generated from X_{STO} consumption and more X_{STO} was left for denitrification in first anoxic period of set 3 during which S_{S} was exhausted and X_{STO} was the main source of UAP. While, during the same time span, set 1 was under aerobic condition, it generated more SMP and less X_{STO} left for denitrification. During anoxic period of set 1 (a little later after aeration pause), no significant denitrification happened, which was probably due to the following assumptions: (a) readily biodegradable carbons, e.g., X_{STO} and S_{S} , had been consumed and could not provide electron donors for rapid denitrification (Fig. 2b, c), (b) SMPs are slowly biodegradable organic matter (Rittmann et al. 1987) making denitrification relevantly slow, and (c) endogenous denitrification rate is lower than exogenous denitrification rate (Henze et al. 2000; Majone et al. 1998).

The same explanation could be used to interpret the reason that set 2 generated approximately 57% less SCOD and consumed 58% more S_{NO} , compared with traditional SBR cycle (set 1). Since the simulated results showed the residual X_{STO} in set 2 was almost the same as in set 1 (Figs. 2c and 3c), therefore it demanded less DO than set 1. This could interpret the phenomenon that the DO concentration did not reduce to 0 in an hour after last aeration pause and was higher than that in set 1.

As the simulations showed in Figs. 2c, 3c, and 4c, there were few X_{STO} prediction in cycle end, compared with ASM3 and other modified ASM3 models giving large deviation of X_{STO} predictions (Gujer et al. 1999; Karahan-Gül et al. 2003; Oliveira-Esquerre et al. 2006). The experimental phenomenon, i.e., DO variations, could efficiently and successfully support this result, which means the kinetics of SSSG process in the proposed model is indirectly validated and reasonable.

Hence, according to above discussions, it is suggested that a pre-non-aeration period should be included in this SBR system to control and optimize nitrogen removal and effluent SCOD. Furthermore, the aeration time should not be too long to minimize effluent SCOD and energy cut-short.

In conclusion, a new kinetic model for simulating carbon-based metabolism was successfully established. The proposed model was focused on evaluating SMP formation and degradation and SSSG processes under aerobic and anoxic conditions. Under feast condition, three carbon metabolic pathways were involved: (a) biomass direct growth on one part of substrate; (b) biomass storage of the other substrate; and (c) biomass simultaneous growth on X_{STO} . Consequently, a new kinetic expression for growth on X_{STO} process was developed to describe the degradation of storage products. The main advantage of this study is that it has also provided a comprehensive understanding of the activated sludge process and given a better description for the important relationship between carbon metabolic mechanisms and nitrogen removal. Hence, it is expected to be capable of optimizing activated sludge processes in treatment facility design and/or guiding wastewater treatment plant operation using this new proposed model.

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