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A Thermodynamic Analysis of the Activated Sludge Process: Application to Soybean Wastewater Treatment in a Sequencing Batch Reactor

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A bioenergetic methodology was integrated with a modified activated sludge model No.1 (ASM1) to analyze the activated sludge process, with the treatment of soybean-processing wastewater as an example. With the bioenergetic methodology established by McCarty and coworkers, the microbial yield was predicted and the overall stoichiometrics for biological reactions involving the key chemical and biological species in activated sludge were established. These obtained parameters were related to the ASM1 model, which was modified after coupling the biological reactions in activated sludge with electron balances. This approach was able to approximately describe the treatment of soybean wastewater by activated sludge in a sequencing batch reactor in terms of substrate utilization, biomass growth, and the elector acceptor consumption. Such an attempt provides useful information for accurate modeling of the complex activated sludge process. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 2737–2745, 2009
Keywords: activated sludge model No.1, bioenergetics, degradation, free energy, model, thermodynamic, yield

Introduction

The activate sludge model No.1 (ASM1), established by the International Water Association, was a basis for modeling of activated-sludge-based wastewater treatment systems.[1] In this model, the wide variety of organic carbon and nitrogenous compounds are subdivided into a limited number of fractions based on biodegradability and solubility considerations. The ASM is being widely used to design and assess control strategies for various activated sludge systems.[2–6]

Accurate microbiological modeling requires evaluation of the effects of biological reactions on all important chemical and biological species in the activated sludge system.[7] The ASM requires a large number of empirical parameters, which are difficult to determine. Moreover, many important chemical and biological species are lumped into one assumed model component or one empirical process.[1,8] To sort out these problems, a thermodynamic analysis of the biological synthesis in activated sludge could be performed and the stoichiometrics could be more accurately estimated with the cell yield derived from thermodynamic considerations of the flows of energy and electrons in the catabolic and anabolic pathways. The microbial yield is fundamental to predicting the overall stoichiometrics of the growth/utilization reactions in microbial systems.[7] Since 1960's, McCarty had established a bioenergetic methodology to determine the energy and electron balances in microbial degradation systems such as activated sludge.[9–12] This methodology has been found to be useful for designing and understanding the overall process in biological wastewater treatment systems.[7–8]

In the present work, the bioenergetic methodology established by McCarty was integrated with a modified ASM1 to formulate a new approach to analyze the activated sludge process. The microbial yield was estimated and the overall

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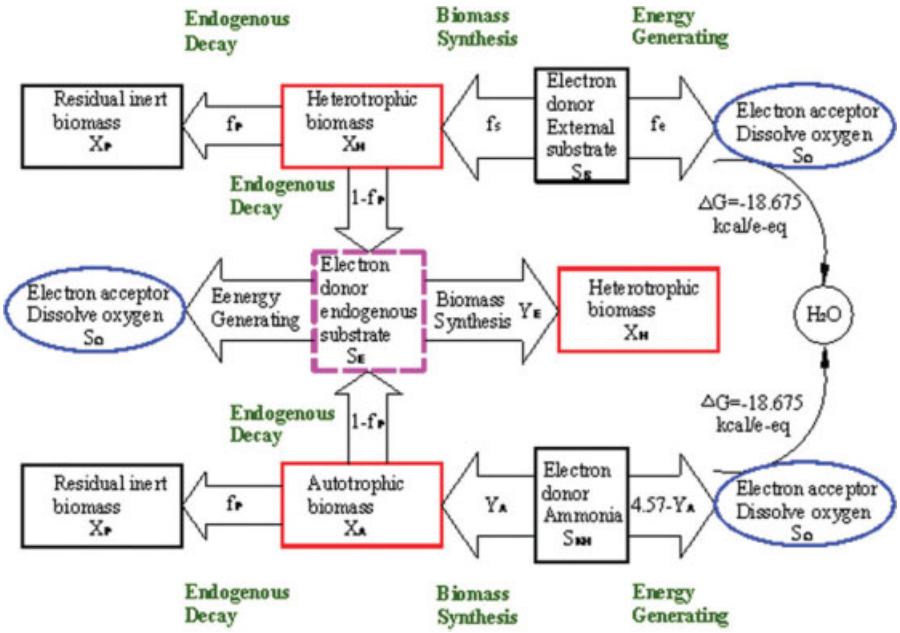

Figure 1. Framework of the new approach to analyze activated sludge process.

fs and *fe* are the fraction of electrons released from the donor substrate that go to cell synthesis and energy generation, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

stoichiometrics for the key chemical and biological species in the system were established by using the bioenergetic method. Then, they were incorporated into the ASM1 which was modified after coupling the biological reactions with electron balances. The performance of a sequencing batch reactor (SBR) for the treatment of soybean wastewater was simulated with this established approach. The dynamic profiles of chemical species in the reactor were also measured and simulated.

Model Development

Bioenergetic methodology

In the bioenergetic methodology established by McCarty,[9–12] for mineralization reactions, all the electrons present in the electron-donor substrate were sent either to the acceptor (f_e) or to biomass synthesis (f_s) as shown in Figure 1. The values of f_e and f_s were coupled through the electron balance, i.e., the sum of f_e and f_s must be equal to 1:

$$f_e + f_s = 1 \tag{1}$$

$$A = \frac{f_e}{f_s} = -\frac{\frac{\Delta G_p^{0'}}{K^m} + \Delta G_{cells}^{0'} + \frac{\Delta G_n^{0'}}{K}}{K\Delta G_R^{0'}} \tag{2}$$

$$f_s = \frac{1}{1+A} \text{ and } f_e = \frac{A}{1+A} \tag{3}$$

in which $\Delta G_R^{0'}$ is the standard free energy of the energy-generating reaction; K is the efficiency of energy capture in the energy-generation reaction; f_e is the fraction of electron-donor electron equivalents sent to the acceptor to drive the energy-generating reaction; and f_s is the fraction of electron-donor electron equivalents invested in biomass via the synthesis reaction. The ratio of f_e/f_s could be defined as A. $\Delta G_p^{0'}$ is the energy consumed to transform the carbon source to pyruvate, $\Delta G_n^{0'}$ is the energy consumed to transform the nitrogen source to NH_4^+, and $\Delta G_{cells}^{0'}$ is the energy consumed to transform common cell intermediates (assumed to be at the energy level of pyruvate and ammonia) to cell biomass.

For the heterotrophic growth under optimum conditions, K varies from 0.4 to 0.8 with an average of 0.60.[7] The amount of energy required to transform ammonia and pyruvate (intermediate) into one equivalent of biomass ($\Delta G_{cells}^{0'}$) is 7.5 kcal/e-eq.[9,12] The exponent m is either $+1$ or -1, depending on whether energy is released (-1) or required ($+1$) for a reaction. The half-reactions for conversion of various forms of inorganic nitrogen into ammonia are used to determine $\Delta G_n^{0'}$. As sufficient ammonia nitrogen is present, $\Delta G_n^{0'} = 0$.

In the overall reaction stoichiometry half-reactions are combined.[11] Utilizing $C_5H_7O_2N$ for cells and assuming that the cells are formed from carbonate and ammonium,[3] the case of soybean wastewater treatment was shown in this work, with $CH_{1.5}O_{0.31}N_{0.25}$ for proteins and CH_2O for carbohydrates.[3]

$$\frac{8}{33}CO_2 + \frac{2}{33}NH_4^+ + \frac{31}{33}H^+ + e^- \rightarrow \frac{8}{33}CH_{1.5}O_{0.31}N_{0.25} + \frac{27}{66}H_2O \tag{4}$$

$$\frac{1}{4}CO_2 + H^+ + e^- \rightarrow \frac{1}{4}CH_2O + \frac{1}{4}H_2O \tag{5}$$

Reactions 4 and 5 indicate that full mineralization of proteins and carbohydrates yields 4.125 e-eq^{-1} mol of the

Table 1. The Modified ASM1

Component Process	S_O O_2	S_{NH} N	S_{NO} N	S_E COD	S_S COD	X_P COD	X_A COD	X_H COD	Kinetics rate expression
Heterotrophic									
Growth on exogenous substrate	$-\frac{1-Y_H}{Y_H}$	$-i_{XB}$			$-\frac{1}{Y_H}$			1	$\mu_H \frac{S_S}{K_S+S_S} \frac{S_O}{K_{O,H}+S_O} X_H$
Growth on endogenous substrate	$-\frac{1-Y_E}{Y_E}$	$-i_{XB}$		$-\frac{1}{Y_E}$				1	$\mu_H \frac{S_E}{K_S+S_E} \frac{S_O}{K_{O,H}+S_O} X_H$
Endogenous decay				$1-f_P$		f_P		−1	$b_H X_H$
Autotrophic									
Growth	$-\frac{4.57-Y_A}{Y_A}$	$-i_{XB}-\frac{1}{Y_A}$	$\frac{1}{Y_A}$				1		$\mu_A \frac{S_{NH}}{K_{NH}+S_{NH}} \frac{S_O}{K_{O,A}+S_O} X_A$
Endogenous decay				$1-f_P$		f_P	−1		$b_A X_A$

former and 4 e-eq^{-1} mol of the latter, respectively. The oxidation of proteins and carbohydrates also yields free energy. Oxidation of proteins and carbohydrates as electron donors respectively produces 7.7 kcal ($\Delta G^{0'} = -7.7$ kcal e^{-1}-eq) and 10 kcal ($\Delta G^{0'} = -10$ kcal e^{-1}-eq) of energy per electron equivalent at pH 7.0.

Biological reaction model

In the present work, the ASM1 was modified through introducing the concept of endogenous decay-regeneration (see Figure 1). This modified ASM1 is given in matrix form in Table 1. In addition to the external substrate, the substrate released from endogenous decay was utilized for heterotrophic growth with a special biomass yield. The endogenous yield factor (Y_E) was not the same as the yield factor from the exogenous substrate (Y_H) as in the original ASM1.[8] This modified model had eight model components to describe the biological reactions, i.e., heterotrophic microorganisms (X_H), autotrophic microorganisms (X_A), exogenous substrate (S_S), residual inert biomass (X_P), ammonia (S_{NH}), nitrate (S_{NO}), endogenous substrate (S_E), and dissolved oxygen (S_O). The units for all organic species were oxygen demand or oxygen (for DO), which is directly proportional to electron equivalents (i.e., 8 g O_2 per e$^-$ equivalent).

An increase in volatile suspended solids (VSS) was the sum of biomass and residual inert biomass accumulations:

$$\frac{d\text{VSS}}{dt} = \frac{dX_H}{dt} + \frac{dX_P}{dt} + \frac{dX_A}{dt} \tag{6}$$

$$\frac{dX_H}{dt} = (\mu_1 + \mu_2)X_H - b_H X_H \tag{7}$$

$$\frac{dX_P}{dt} = f_P(b_H X_H + b_A X_A) \tag{8}$$

$$\frac{dX_A}{dt} = \mu_3 X_A - b_A X_A \tag{9}$$

$$\mu_1 = \mu_H \frac{S_S}{K_S + S_S} \frac{S_O}{K_{O,H} + S_O} \tag{10}$$

$$\mu_2 = \mu_H \frac{S_E}{K_S + S_E} \frac{S_O}{K_{O,H} + S_O} \tag{11}$$

$$\mu_3 = \mu_A \frac{S_{NH}}{K_{NH} + S_{NH}} \frac{S_O}{K_{O,A} + S_O} \tag{12}$$

where $\frac{d\text{VSS}}{dt}$ is the rate of VSS accumulation, $\frac{dX_H}{dt}$ is the rate of heterotrophic biomass accumulation, $\frac{dX_A}{dt}$ is the rate of autotrophic biomass accumulation, $\frac{dX_P}{dt}$ is the rate of residual inert biomass accumulation, μ_1 is the biomass growth rate on S_S, μ_2 is the biomass growth rate on S_E, μ_H is heterotrophic the maximum biomass growth rate, b_H is heterotrophic endogenous decay rate, μ_A is the maximum autotrophic biomass growth rate, b_A is autotrophic endogenous decay rate, $K_{O,H}$ is the dissolve oxygen affinity constant of X_H, $K_{O,A}$ is the dissolve oxygen affinity constant of X_A, f_P is fraction of residual inert biomass COD formed from endogenous decay.

The substrate (SCOD) removal rate was the sum of the exogenous (S_S) and endogenous substrate (S_E) removal rates as follows:

$$\frac{d\text{SCOD}}{dt} = \frac{dS_S}{dt} + \frac{dS_E}{dt} = -\frac{1}{Y_H}\mu_1 X_H - \frac{1}{Y_E}\mu_2 X_H + (1 - f_P)b_H X_H \tag{13}$$

where $\frac{d\text{SCOD}}{dt}$ is the rate of substrate removal, $\frac{dS_S}{dt}$ is the rate of exogenous substrate removal, $\frac{dS_E}{dt}$ is the rate of endogenous substrate removal.

The ammonia removal rate and nitrate production rate were described with the following equations:

$$\frac{dS_{NH}}{dt} = -i_{XB}\mu_1 X_H - i_{XB}\mu_2 X_H - \left(i_{XB} + \frac{1}{Y_A}\right)\mu_3 X_A \tag{14}$$

$$\frac{dS_{NO}}{dt} = \frac{1}{Y_A}\mu_3 X_A \tag{15}$$

where $\frac{dS_{NH}}{dt}$ is the rate of ammonia removal, $\frac{dS_{NO}}{dt}$ is the rate of nitrate production, i_{XB} is nitrogen content of biomass, and Y_A is the yield factor of autotrophs.

The oxygen uptake rate (OUR or $\frac{dS_O}{dt}$) was the sum of the three respiration processes: utilization of S_S, S_E, and S_{NH}.

$$\text{OUR} = \frac{dS_O}{dt} = -\frac{1-Y_H}{Y_H}\mu_1 X_H - \frac{1-Y_E}{Y_E}\mu_2 X_H - \frac{4.57-Y_A}{Y_A}\mu_3 X_A \tag{16}$$

Materials and Methods

Sludge, wastewater, and reactor

Activated sludge was cultivated in a laboratory-scale SBR, which had a working volume of 2 L. The reactor was

operated at 20°C with 3 min of influent filling, 217 min of aeration, 15 min of settling, and 5 min of effluent withdrawal from the reactor. Air was applied to the SBR at a flow rate of 0.4 $m^3\ h^{-1}$, equivalent to a superficial up-flow velocity of 2.8 cm s^{-1}. The DO concentration in aerobic phase during SBR operation was above 4 mg L^{-1}. The desired SRT was set by controlling the amount of sludge wasted from the SBR in each cycle. In this work, the SRT for the SBR operation was designed at 20 days, and the initial MLVSS concentration of the SBR was ~2000 mg L^{-1}.

The SBR was fed with a soybean-processing wastewater, collected from a local soybean-processing plant, at a soluble chemical oxygen demand (COD) of around 800 mg L^{-1}. The raw wastewater was diluted 10 times using tap water to obtain the influent for the SBR. It contained a sufficient amount of nitrogen with an ammonia concentration of 150 mg N L^{-1}. Phosphorus was added as Na_2HPO_4 to ensure the ratio of COD to P to be 100:1 by mass in the influent. In addition, a microelement solution was supplied to produce influent concentrations of (in μg/L): H_3BO_3, 50; $ZnCl_2$, 50; $CuCl_2$, 30; $MnSO_4 \cdot H_2O$, 50; $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 50; $AlCl_3$, 50; $CoCl_2 \cdot 6H_2O$, 50; and $NiCl_2$, 50. The influent pH value was adjusted to 7.0 through the dose of $NaHCO_3$ or HCl.

Experiments

A primary source of quantitative data used for a long-term reactor performance simulation was the routine measurements everyday for the SBR. The samples were analyzed for the COD, NH_4^+-N, and mixed liquid volatile suspended solid (MLVSS) concentrations.

In addition to the long-term SBR operation, batch experiments were also conducted to evaluate the established approach. Sludge was sampled from the SBR when no substrate was present in the medium. The 2-L batch reactors were inoculated with the activated sludge and continuously aerated until the DO concentration exceeded 4 mg L^{-1} for complete nitrification. Then, the external substrate, i.e., the soybean-processing wastewater, at a pre-determined concentration after dilution was dosed and the oxygen uptake rate (OUR) was monitored until the substrate became depleted and the endogenous activity was resumed. The initial external substrate in the batch reactor was ~220 mg L^{-1}. Samples were taken every 5–10 min for analysis. The tests were conducted at 20°C and pH 7.0.

Analysis

The DO concentration in the SBR was measured with a DO electrode (MO128, Mettler-Toledo Gmbh, Switzerland). The OUR was measured according to Keesman and Spanjers.[4] The OUR was measured using a respirometer. The respirometer consisted of a 300-mL glass vessel with a pot at the top for insertion of a DO probe (MO128, Mettler-Toledo Gmbh, Switzerland). A magnetic stirring bar and a stirring plate provided internal mixing of the liquor and sludge. For each respirometric test, 250 mL of sludge was collected from the reactors and added to the respirometer. The slope of the DO concentration decline was measured in 15 min. The OUR was calculated from the slope though linear regression. The OUR values were determined twice for each test and the averages are reported in this article. The carbohydrates were determined as glucose equivalent using enthrone-sulfuric acid method,[13] whereas the proteins were measured as bovine albumin equivalent using the Lowry method.[14] Measurement of COD, NH_4^+-N, mixed liquor suspended solids (MLSS), and MLVSS was performed following the Standard Methods.[15]

Results and Discussion

Characterization of soybean-processing wastewater

The raw wastewater contained proteins of 5.50 g L^{-1} and carbohydrates of 7.40 g L^{-1}. Efforts were initially made to estimate the contribution of each organic component to the total COD (TCOD) in this wastewater. For complete oxidation, 32 moles of proteins requires 33 moles of oxygen:

$$32CH_{1.5}O_{0.31}N_{0.25} + 33O_2 \rightarrow 12H_2O + 32CO_2 + 8NH_3 \tag{17}$$

Further calculations give the amount of oxygen required per unit amount of proteins degraded:

$$\frac{33 \text{ mole } O_2}{32 \text{ mole protein}} \times \frac{1 \text{ mole protein}}{22 \text{ g protein}} \times \frac{32 \text{ g } O_2}{1 \text{ mole } O_2} = 1.50 \text{ g } O_2 \text{ g}^1 \text{ proteins} = 1.50 \text{ g COD } g^{-1} \text{ proteins}$$

For 5.50 g L^{-1} proteins in the soybean wastewater,

$$\frac{1.5 \text{ g COD}}{1 \text{ g protein}} \times \frac{5.5 \text{ g protein}}{1 \text{ L wastewater}} = 8.25\ g\text{COD L}^{-1}$$

Therefore, the COD due to the presence of proteins in the wastewater was 8.25 g COD L^{-1}, which was 49.8% of TCOD.

One mole of carbohydrates requires one mole of oxygen for complete oxidation.

$$CH_2O + O_2 \rightarrow H_2O + CO_2 \tag{18}$$

Similarly, an estimate for the oxygen requirement per unit amount of carbohydrates is 1.07 g COD g^{-1} carbohydrates. The following calculations give the amount of oxygen required per unit amount of carbohydrates degraded:

$$\frac{1 \text{ mole } O_2}{1 \text{ mole carbohydrate}} \times \frac{1 \text{ mole carbohydrate}}{30 \text{ g carbohydrate}} \times \frac{32 \text{ g } O_2}{1 \text{ mole } O_2} = 1.07 \text{ g } O_2 \text{ g}^1 \text{ carbohydrates} = 1.07 \text{ g COD } g^{-1} \text{ carbohydrates}$$

For 7.40 g L^{-1} carbohydrates in the wastewater,

$$\frac{1.07 \text{ g COD}}{1 \text{ g carbohydrate}} \times \frac{7.4 \text{ g carbohydrate}}{1 \text{ L wastewater}} = 7.92\ g\text{COD L}^{-1}$$

In a similar way, the COD exerted by carbohydrates in this wastewater was calculated to be 7.92 g COD L^{-1}, which was 47.8% of TCOD.

Based on analyses of organics in the soybean wastewater, it was concluded that the proteins and carbohydrates were

Table 2. Stoichiometrics for the Mineralization of Proteins and Carbohydrates in the Soybean Wastewater

	$CH_{1.5}O_{0.31}N_{0.25}$	CH_2O	O_2	H^+	H_2O	CO_2	NH_4^+	HCO_3^-	$C_5H_7O_2N$
Protein mineralization	−1.0		−0.3701	−0.1193	0.111	0.3372	0.1176		0.132
Carbohydrate mineralization		−1.0	−0.278		0.8556	0.4224	−0.1444	−0.1444	0.1444

the major organic components contributing the TCOD in this wastewater. A total of 97.6% of the TCOD in the wastewater was accounted for by proteins and carbohydrates.

Overall stoichiometry

For the full biodegradation stoichiometry (R), the reactions coupling the electron donor and acceptor were combined with the reactions for cell synthesis using the f_e and f_s values.[11]

For proteins, the released energy (ΔG_{e-R}) could be calculated as follows:

$$\Delta G_R^{0'} = \Delta G_a^{0'} - \Delta G_d^{0'} = -7.7 - 18.675 = -26.375 \text{ kcal e} - \text{eq}^{-1} \quad (19)$$

The energy consumed in cell synthesis (ΔG_{e-S}) was calculated as:

$$\Delta G_{syn}^{0'} = \frac{\Delta G_P^{0'}}{K^m} + \Delta G_{cells}^{0'} + \frac{\Delta G_n^{0'}}{K} = \frac{8.545 - 7.7}{0.6} + 7.5 + 0 = 8.908 \text{ kcal e} - \text{eq}^{-1} \quad (20)$$

$$A = -\frac{\Delta G_{syn}^{0'}}{K \Delta G_R^{0'}} = \frac{8.908}{0.6 \times 26.375} = 0.563 \text{ e} - \text{eq e} - \text{eq}^{-1} \quad (21)$$

According to the bioenergetic methodology, $f_s = 0.640$ e-eq/e-eq, and $f_e = 0.360$ e-eq/e-eq. Normalizing the result to 1 mol of the substrate, the full stoichiometry for the mineralization of proteins was as below:

$$CH_{1.5}O_{0.31}N_{0.25} + 0.1193H^+ + 0.3701O_2 \rightarrow 0.132C_5H_7O_2N + 0.111H_2O + 0.3372CO_2 + 0.1176NH_4^+ \quad (22)$$

Similarly, the full stoichiometry for the mineralization of carbohydrates was as follows:

$$CH_2O + 0.1444HCO_3^- + 0.1444NH_4^+ + 0.278O_2 \rightarrow 0.1444C_5H_7O_2N + 0.8556H_2O + 0.4224CO_2 \quad (23)$$

Table 2 summarizes the mole-based stoichiometric coefficients for the two reactions, where a negative value indicates a reactant and a positive sense indicates a product.

Exogenous heterotrophic biomass yield

The theoretical biomass yield is a stoichiometric constant which relates only to the growth mechanisms and is not affected by the growth reaction rate.[16] It could be evaluated through electron equivalent without the interference of endogenous metabolism.[11] The evaluation process involves the stoichiometry of the electron donor and acceptor, the free energy released per unit electron transferred, different biochemical pathways responsible for the electron transfer, energy utilization, and the corresponding energy transfer efficiencies. Therefore, the microbial yield could be predicted with a thermodynamic method.[16–19] The f_s value determined using the electron and energy balances could be used to predict the theoretical biomass yield (Y) in the following pathway[7]:

$$\frac{\text{Ymol cells}}{\text{mol substrate}} = f_s \times \frac{\text{mol cells}}{\text{EQC e}^-\text{eq}} \times \frac{\text{EQS e}^-\text{eq}}{\text{mol substrate}} \quad (24)$$

where EQS is the electron equivalents available per mole of substrate and EQC is the electron equivalents required to synthesize cells.

To calculate the values of EQC and EQS, the stoichiometry was predicted based on the structured overall reaction, assuming that ammonia was the nitrogen source for cell synthesis:

$$CH_mO_lN_k + aNH_3 + bO_2 \rightarrow y_cCH_pO_nN_g + cH_2O + dCO_2 \quad (25)$$

where $CH_mO_lN_k$ is the carbon-source electron-donor formula, $CH_pO_nN_g$ is the cell formula, y_c is the fraction of the substrate carbon converted to biomass (the carbon yield of cells), and a, b, c, d are the stoichiometric coefficients for the other compounds in the reaction.

The degree of reductance of carbon in the substrate (γ_s) and the degree of reductance of carbon in cells (γ_c) could be computed from the following equations. Then, EQS and EQC were equivalent to γ_s and γ_c when the cells and carbon source are written in terms of 1 C-mol.

$$\gamma_s = 4 + m - 2l - 3k \quad (26)$$

$$\gamma_c = 4 + p - 2n - 3g \quad (27)$$

In the present work, EQC was 20 when $C_5H_7O_2N$ is selected as a cell formulation. The EQS was 4.125 for proteins and 4 for carbohydrates. With Eq. 24, the theoretical biomass yields for growth on proteins (Y_1) and carbohydrates (Y_2) were 0.132 mol cells mol^{-1} substrate (i.e., 0.667 mg COD_X mg^{-1} COD_S) and 0.1444 mol cells mol^{-1} substrate (i.e., 0.544 mg COD_X mg^{-1} COD_S), respectively. Thus, from the characterization results of the soybean wastewater for the fractionation of proteins and carbohydrates, the biomass yields for growth on this wastewater (Y_H) was estimated to be 0.607 mg COD_X mg^{-1} COD_S.

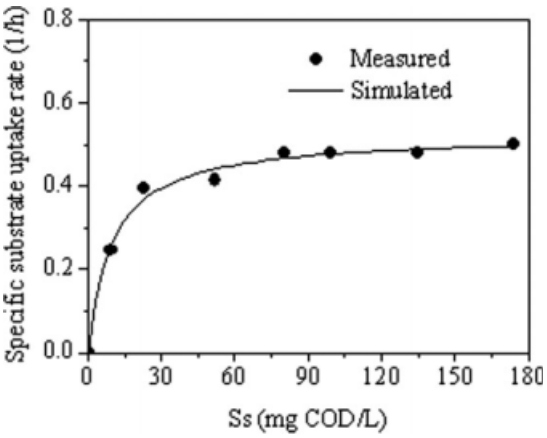

Figure 2. Plot of substrate uptake rate vs. substrate concentration to determine the specific maximum growth rate on substrate (μ_H) and the substrate half-saturation constant.

Biological reaction parameters

The specific maximum growth rate on substrate (μ_H) and the substrate half-saturation coefficient (K_S) were experimentally determined following Henze et al.[20] The increase in the substrate uptake rate with the increasing S_S concentration is depicted in Figure 2. The experiments were carried out with dose of substrate at various levels to the endogenous sludge, resulting in various substrate uptake rates, i.e., exogenous respiration rates, up to a maximum rate. The parameters μ_H and K_S could be estimated by fitting the curve in Figure 2. The changing pattern was well described with a high correlation coefficient of 0.9914. The μ_H and K_S were determined to be 0.35 h^{-1} and 9.8 g COD m^{-3}, respectively.

Y_E is the net biomass yield from growth on the endogenously released substrate. Biomass is the substrate and it would be partially oxidized for energy, while the remaining portion is re-synthesized. The yield in the endogenous substrate resynthesis depends on the state of reduction of nitrogen in the system. If ammonia is in abundance, the approach outlined by Droste could be adopted.[8] The determination of Y_E followed the procedure for determining Y_H with the pyruvate as electron donor for the half reactions (see Eq. 28). The utilization of 1 g COD of the endogenously released substrate in the biomass decay process would yield 0.648 g COD of re-synthesized biomass, i.e., $Y_E = 0.648$ mg COD_X mg^{-1} COD_S. The ultimate accumulation of endogenous residual inert biomass is usually ~20% of the newly produced biomass.[21] Typical values for f_P and b_H are 0.08 and 0.62 d^{-1}, respectively.[20] Table 3 shows all the parameters used in our modified model, their symbols, and their units.

$$\frac{1}{10}CH_3COCOO^- + \frac{2}{5}H_2O \rightarrow \frac{1}{5}CO_2 + \frac{1}{10}HCO_3^- + H^+ + e \quad (28)$$

Modeling the treatment of soybean wastewater

Figure 3 compares the simulated and measured results for the OUR, MLVSS, NH_4^+-N and soluble COD in the batch tests. The initial concentration of active biomass was estimated using the baseline endogenous OUR prior to the substrate addition. The maximum difference between the measured and calculated values was 20%, and 65% of the results had a difference of less than 5%. Furthermore, the model shows no systematic deviations. Model results matched the experimental data for the four parameters. After the dose of substrate, the OUR increased because of the rapid oxidation of the external substrate, while part of the electron flow went directly to respiration (Figure 3A). The sharp bending point in the OUR curve corresponded with the complete removal of the exogenous substrate dosed (Figure 3B). The soluble COD concentration decreased rapidly and continuously in the initial half hour (Figure 3B), as the external substrate was consumed. The NH_4^+-N consumption exhibited a lag time, attributed to a relatively low oxidation rate of the autotrophs (Figure 3C). The MLVSS initially increased from 720 to 850 mg/L in the initial half hour, but later decreased gradually to 830 mg/L at 4 h (Figure 3B).

The model was also evaluated by simulating the long-term SBR operation results of 200 days. Figure 4 compares the simulation and experimental results for the MLVSS and effluent COD and NH_4^+-N concentrations. Similarly, the average difference between the measured and calculated values was 12% and the model shows no systematic deviations. Thus, the model was able to simulate all these variations well. Such a good agreement between the measured and

Table 3. Parameters Used in the Modified ASM1

Parameter	Definition	Values	Unit	Sources
Y_H	yield coefficient for X_H growth on S_S	0.607	g COD g^{-1} COD	This work
Y_E	yield coefficient for X_H growth on S_E	0.648	g COD g^{-1} COD	This work
Y_A	yield coefficient for X_A growth	0.24	g COD g^{-1} COD	Henze et al.[20]
f_P	fraction of X_P in respiration	0.08	g COD g^{-1} COD	Henze et al.[20]
i_{XB}	nitrogen content of biomass	0.086	g N g^{-1} COD	Henze et al.[20]
μ_H	maximum growth rate of X_H on S_S	8.4	d^{-1}	This work
K_S	biomass affinity constant for S_S	9.8	g COD m^{-3}	This work
$K_{O,H}$	dissolve oxygen affinity constant of X_H	0.20	g O_2 m^{-3}	Henze et al.[20]
b_H	respiration rate coefficient of X_H	0.62	d^{-1}	Henze et al.[20]
μ_A	maximum growth rate of X_A	0.8	d^{-1}	Henze et al.[20]
b_A	respiration rate coefficient of X_A	0.15	d^{-1}	Henze et al.[20]
$K_{O,A}$	oxygen affinity constant for X_A	0.4	g O_2 m^{-3}	Henze et al.[20]
K_{NH}	biomass S_{NH} affinity constant	1.0	g N m^{-3}	Henze et al.[20]
f_e	the electron-donor substrate are sent to the electron-acceptor	0.36* 0.278†	e-eq e^{-1}-eq	This work
f_s	the electron-donor substrate are sent to the biomass synthesis	0.64* 0.722†	e-eq e^{-1}-eq	This work

*For proteins.
†For carbohydrates.

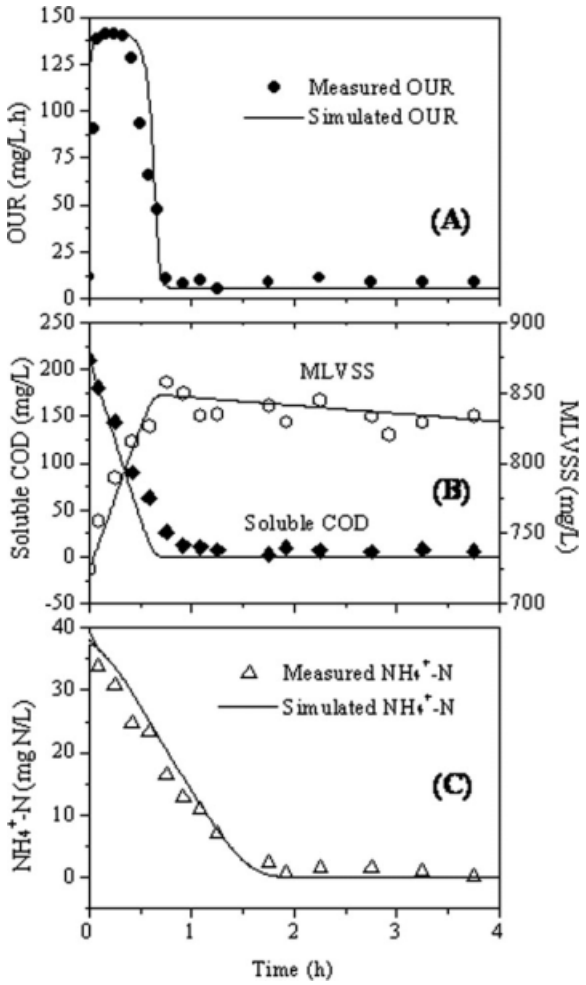

Figure 3. Model evaluation of the experimentally measured OUR, NH_4^+-N, soluble COD data and MLVSS profiles in batch tests (Line for model prediction, and symbols for experimental measurement).

predicted results suggests the validity of the model established in this work. The modeling results show that the effluent COD and NH_4^+-N take about 30 days to approach their plateaus. On the other hand, the MLVSS needed a long run (at least 100 days) to reach its plateau. At steady-state, the active microorganisms were about 30% of MLVSS. The remaining biomass was comprised of inert biomass.

Analysis of the degradation process

Biological degradation of wastewater by activated sludge is always achieved through multiple-substrate utilization for complete mineralization. These multiple substrates utilization might proceed at different rates, and thus prediction of the microbial growth and the elimination of degradable substrates in such systems require an accurate method for modeling. In our approach, determination of the rate of substrate utilization was coupled to the stoichiometry, which was linked to our modified ASM1 model. Therefore, the kinetic biodegradation routine could predict rates for all species in the degradation reaction and returned changes to the total concentration of each affected species.

The substrate utilization rate for each electron-donor substrate in the soybean wastewater was coupled with the stoichiometry shown in Table 2 to predict the concentration changing rate of all reactants and products. Figure 5 shows the model predictions for the profiles of proteins ($CH_{1.5}O_{0.31}N_{0.25}$), carbohydrates (CH_2O), cells ($C_5H_7O_2N$), H^+, NH_4^+, HCO_3^- and released CO_2 from the heterotrophic growth in the degradation process of soybean wastewater. It should be noted that the species profiles here were the relative dynamic variations attributed to the degradation process, rather than their absolute concentrations. The initial values for H^+, NH_4^+, HCO_3^-, and CO_2 were set at zero, and the negative values indicate their consumption. Because of the rapid consumption of substrate by the active cells for new synthesis, the concentration of $CH_{1.5}O_{0.31}N_{0.25}$ decreased sharply and down to zero within half hour (Figure 5A). The concentration of CH_2O exhibited a decreasing trend (Figure 5A) attributed to the variation of the concentration of cells ($C_5H_7O_2N$). In addition, the carbohydrates in the soybean wastewater of this work were a polymer, rather than a simple sugar. Therefore, their consumption rate was assumed to be slower than that of proteins. In initial half hour, the active cells utilized the external substrate for growth. The content of active cells increased because of the rapid consumption of the external substrate (Figure 5B). The increasing rate of cells in this phase was greater than the subsequent phase, in which CH_2O was the only external substrate (Figure 5A).

Both reactions 22 and 23 released CO_2 when $CH_{1.5}O_{0.31}N_{0.25}$ and CH_2O were consumed by cells (Figure 5B). Formation of NH_4^+ occurs only when $CH_{1.5}O_{0.31}N_{0.25}$ was being utilized. The NH_4^+ concentration increases initially in the rapid microbial $CH_{1.5}O_{0.31}N_{0.25}$ consumption period.

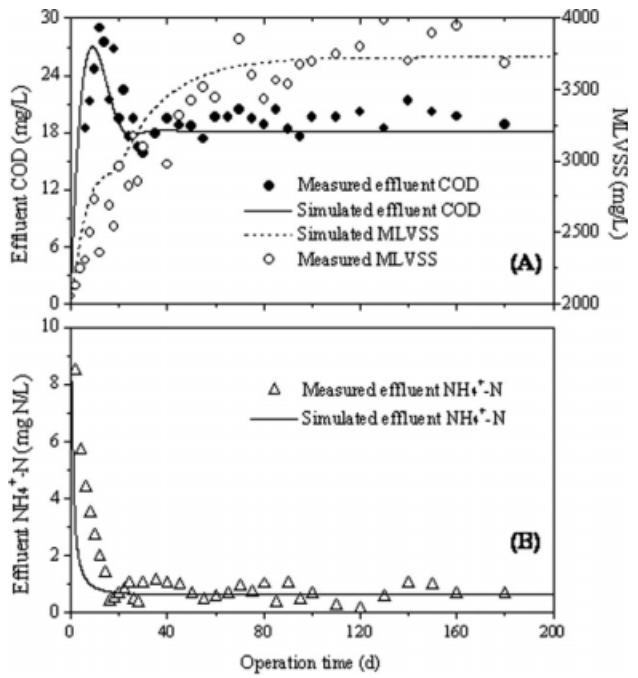

Figure 4. Model evaluation of the long-term operational performance of the SBR in terms of effluent COD and NH_4^+-N concentrations as well as MLVSS profiles.

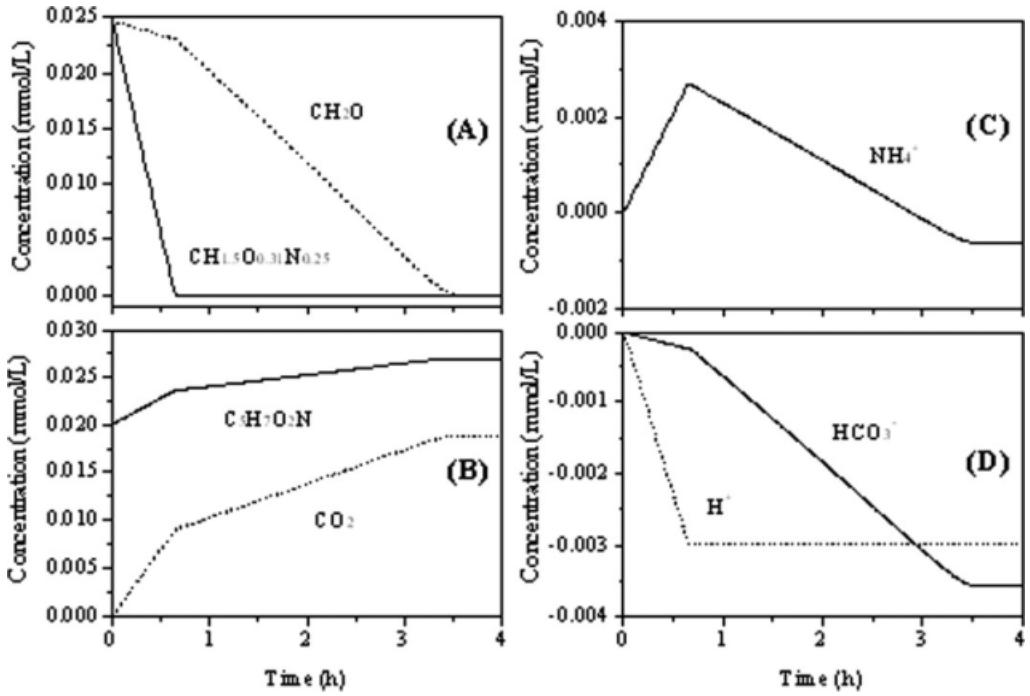

Figure 5. Model simulation for the profiles of proteins ($CH_{1.5}O_{0.31}N_{0.25}$), carbohydrates (CH_2O), cells ($C_5H_7O_2N$), released CO_2, NH_4^+, HCO_3^-, and H^+ for the heterotrophic growth in soybean wastewater treatment.

After the depletion of $CH_{1.5}O_{0.31}N_{0.25}$, NH_4^+ is utilized by cells for growth on CH_2O, resulting in a decline of NH_4^+ concentration (Figure 5C). A linear decrease in H^+ concentration occurs in the $CH_{1.5}O_{0.31}N_{0.25}$-consumption phase because of the microbial assimilation of H^+ (Reaction 22). In the CH_2O-consumption phase, the H^+ concentration did not change further (Figure 5D). The HCO_3^- concentration decreased continually when CH_2O was consumed at an increasing rate. Thus, the variation of HCO_3^- concentration was similar to that of CH_2O concentration (Figure 5D). These results clearly illuminate the overall bioreaction processes in the degradation of soybean wastewater.

In summary, the approach developed in this work through integrating the thermodynamic methodology and a modified ASM1 was able to precisely describe the treatment of soybean wastewater by activated sludge in an SBR, in terms of substrate utilization, biomass growth, and elector acceptor consumption. The effects of biological reactions on all important chemical and biological species in the system, i.e., the dynamic profiles of cells, H^+, NH_4^+, HCO_3^-, and release of CO_2, could be simulated well with this new approach. Hopefully, information provided in this article might be useful for more accurate modeling of wastewater treatment processes.

Conclusions

A bioenergetic model for wastewater treatment was developed using the thermodynamic methodology combined with a modified ASM1. A systematic method for developing reaction stoichiometry for waste biodegradation reactions was used, and the thermodynamic methodology was applied to evaluate the coefficients for the true biomass yield from substrate. The obtained parameters were related to the ASM1 model, which coupled biological reactions with bioenergetics. The established model was applied to the treatment of a soybean-processing wastewater in an SBR. The model was able to accurately describe the consumption of substrate, the accumulation of MLVSS, and the OUR profiles in the wastewater treatment process and the long-term operation results of the SBR. Model simulation results clearly show the variations of $C_{16}H_{24}O_5N_4$, CH_2O, cells ($C_5H_7O_2N$), H^+, NH_4^+, HCO_3^- concentration, and the release of CO_2.

Acknowledgments

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Notation

A = the ratio of f_e/f_s
ASM = activated sludge model
ASM1 = activated sludge model no. 1
b_A = autotrophic endogenous decay rate, h^{-1}
b_H = heterotrophic endogenous decay rate, h^{-1}
COD = chemical oxygen demand, mg O_2 L^{-1}
DO = dissolved oxygen, mg O_2 L^{-1}
EQC = electron equivalents in one mole of biomass (e-eq mol^{-1})
EQS = electron equivalents in one mole of substrate (e-eq mol^{-1})
f_e = the fraction of electron-donor electron equivalents sent to the acceptor to drive the energy-generating redox reaction
f_P = the fraction of residual inert biomass formed from endogenous decay
f_s = the fraction of electron-donor electron equivalents invested in biomass via the synthesis reaction
$\Delta G^{0'}$ = standard free energy for the electron donor reduction half-reduction (kcal e^{-1}-eq)
$\Delta G_a^{0'}$ = standard free energy for the electron acceptor reduction half reaction (kcal e^{-1}-eq)

$\Delta G_R^{0'}$ = standard free energy of the energy generating redox couple (kcal e^{-1}-eq)
$\Delta G_d^{0'}$ = standard free energy for the electron donor reduction half reaction (kcal e^{-1}-eq)
$\Delta G_{syn}^{0'}$ = standard free energy of the cell synthesis reaction (kcal e^{-1}-eq)
$\Delta G_P^{0'}$ = standard free energy to convert the carbon source to the biological intermediate, pyruvate
$\Delta G_{cells}^{0'}$ = standard free energy to synthesize macromolecules (kcal e^{-1}-eq)
$\Delta G_n^{0'}$ = the energy consumed to transform the nitrogen source to NH_4^+ (kcal e^{-1}-eq)
i_{XB} = nitrogen content of biomass, g N g^{-1} COD
K = the efficiency of energy capture in the energy-generation reaction
K_S = substrate affinity constant, g COD m^{-3}
K_{NH} = biomass S_{NH} affinity constant, g N m^{-3}
$K_{O,A}$ = oxygen affinity constant for X_A, g O_2 m^{-3}
$K_{O,H}$ = dissolve oxygen affinity constant of X_H, g O_2 m^{-3}
MLSS = mixed liquor suspended solids, mg L^{-1}
MLVSS = mixed liquor volatile suspended solids, mg L^{-1}
OUR = oxygen uptake rate, mg O_2 $L^{-1}h^{-1}$
R = full biodegradation stoichiometry
SBR = sequencing batch reactor
SCOD = soluble chemical oxygen demand, mg O_2 L^{-1}
SRT = solids retention time, d
S_E = endogenous substrate, mg COD L^{-1}
S_O = dissolved oxygen, mg O_2 L^{-1}
S_{NH} = ammonia, mg N L^{-1}
S_{NO} = nitrate, mg N L^{-1}
S_S = exogenous substrate, mg COD L^{-1}
TCOD = total chemical oxygen demand, mg O_2 L^{-}
μ_1 = the biomass growth rate on S_S, h^{-1}
μ_2 = the biomass growth rate on S_E, h^{-}
μ_3 = the autotrophic biomass growth rate, h^{-1}
μ_A = the autotrophic maximum growth rate, h^{-1}
μ_H = the heterotrophic maximum growth rate, h^{-1}
VSS = volatile suspended solids, mg L^{-1}
X_A = concentration of autotrophic microorganisms, mg COD L^{-1}
X_H = concentration of heterotrophic microorganisms, mg COD L^{-1}
X_P = residual inert biomass, mg COD L^{-1}
Y_1 = theoretical biomass yields for growth on proteins, g COD g^{-1} COD
Y_2 = theoretical biomass yields for growth on carbohydrates, g COD g^{-1} COD
Y_A = yield coefficient for autotrophic growth, g COD g^{-1} COD
Y_E = yield coefficient for growth on endogenous substrate, g COD g^{-1} COD
Y_H = yield coefficient for growth on exogenous substrate, g COD g^{-1} COD

Literature Cited

1. Henze M, Gujer W, Mino T, van Loosdrecht MCM. Activated Sludge Models ASM1, ASM2, ASM2d, and ASM3. IWA Scientific and Technical Report No. 9. IWA Publishing, London, UK, 2000.
2. Keesman KJ, Spanjers H, van Straten G. Analysis of endogenous process behavior in activated sludge. *Biotechnol Bioeng*. 1998;57: 155–163.
3. Grady CPL Jr, Glen TD, Henry CL. *Biological Wastewater Treatment*, 2nd ed. Basel, Switzerland: Marcel Dekker, Inc, 1999.
4. Keesman KJ, Spanjers H. Endogenous model state and parameter estimation from an extensive batch experiment. *Biotechnol Bioeng*. 2000;68:422–429.
5. Smets IY, Haegebaert JV, Carrette R, van Impe JF. Linearization of the activated sludge model ASM1 for fast and reliable predictions. *Water Res*. 2003;37:1831–1851.
6. Su KZ, Yu HQ. A generalized model for aerobic granule-based sequencing batch reactor. 1. Model development. *Environ Sci Technol*. 2006;40:4703–4708.
7. van Briesen JM, Rittmann BE. Mathematical description of microbiological reactions involving intermediates. *Biotechnol Bioeng*. 2000;67:35–52.
8. Droste RL. Endogenous decay and bioenergetics theory for aerobic wastewater treatment. *Water Res*. 1998;32:410–418.
9. McCarty PL. *Energetics and bacterial growth*. In: Faust SD, Hunter JV, editors. *Organic Compounds in Aquatic Environments*. New York: Marcel Dekker, 1971.
10. McCarty PL. Energetics and bacterial growth. *The Fifth Rudolf Research Conference, Rutgers*. The State University, New Bruswick, USA, 1969.
11. McCarty PL. Stoichiometry of biological reactions. *Paper presented at the International Conference toward a Unified Concept of Biological Waste Treatment Design*, Atlanta, USA, 1972.
12. McCarty PL. Thermodynamics of biological synthesis and growth. In: Baers J, editor. Advances in Water Pollution Research: Proceedings of the 2nd International Conference on Water Pollution Research. Oxford, England: Pergamon Press, Inc., 1965:169–199.
13. Dubois M, Gilles KA, Hamilton JK, Rebers PA, Smith F. Colorimetric method for determination sugars and related substance. *Anal Chem*. 1956;28:350–356.
14. Lowry OH, Farr AL, Randall RJ. Protein measurement with the folin phenol reagent. *J Biol Chem*. 1951;193:265–275.
15. APHA. *Standard Methods for the Examination of Water and Wastewater*, 19th ed. Washington, DC: American Public Health Association, 1995.
16. Rittmann BE, McCarty PL. *Environmental Biotechnology: Principles and Applications*. New York: McGraw-Hill. 2001:754.
17. Heijnen JJ, van Loosdrecht MCM, Tijhuis L. A black box mathematical model to calculate auto- and heterotrophic biomass yields based on Gibbs energy dissipation. *Biotechnol Bioeng*. 1992;40: 1139–1154.
18. Xiao JH, van Briesen JM. Expanded thermodynamic model for microbial true yield prediction. *Biotechnol Bioeng*. 2006;93:110–121.
19. McCarty PL. Thermodynamic electron equivalents model for bacterial yield prediction: Modifications and comparative evaluations. *Biotechnol Bioeng*. 2007;97:377–388.
20. Henze M, Grady CPL Jr, Gujer W, Marais GVR, Matsuo T. Activated sludge model No. 1. *Scientific and Technical Report No. 1*, IAWPRC, London, 1987.
21. Christensen DR, McCarty PL. Multi-process biological treatment model. *J Water Pollut Control Fed*. 1975;47:2652–2664.

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