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Dimensional analysis for establishing the testing criteria of kinetic study with respirometry

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Abstract The kinetic study of a microbial system requires the determination of kinetic parameters under a set of operating variables. Previous researchers indicated that initial conditions, such as S_o/X_o and S_o/K_s, may influence the reliability of the parameter estimation. However, little study has been done to identify the sensitivity of system variables to the parameter estimation. This study proposes a novel dimensional analysis and identifies six dimensionless groups: μ_m/f_w, k_d/f_w, Y_g, S_o/K_s, K_s/S_o, and $1/(f_w\,\theta_c - 1)$. By incorporating the SP-moving algorithm proposed by Wu and coworkers in 2001, an algorithm was proposed in this study to perform a sensitivity analysis on the six dimensionless groups. Results of this analysis reveal that S_o/X_o is more sensitive than S_o/K_s, as also evidenced by the fact that gross growth yield (Y_g) is sensitive and affecting S_o/X_o. The analysis also suggests that the θ_c-based wasting frequency ($f_w\,\theta_c$) is more sensitive than the daily wasting frequency (f_w). A critical minimum value of 1.3 for S_o/X_o and a maximum value of 0.1 for S_o/K_s were suggested to establish the testing criteria for the kinetic study under the respirometric conditions.

Keywords Dimensional analysis; kinetics; respirometry; testing criteria

Introduction

The four-parameter Monod kinetics has been widely accepted for years (Monod, 1949). In order to calibrate the system parameters, a chemostat (steady state) laboratory procedure is normally conducted at various sludge retention times (SRT, θ_c) to obtain substrate (S) and biomass (X) concentrations. A linearization technique is then used for the calibration, such as the Lineweaver–Burke method ($1/\mu$ vs. 1/S), Hanes method (S/μ vs. S), and Hofstee method (μ vs. μ/S). It has been well recognized that these methods are not reliable (Grady and Lim, 1980). The determination of COD and VSS for the substrate and biomass respectively is time-consuming and subject to inherent errors. Also, the SRT is hardly maintained accurately due to incomplete mixing and vaporization of the testing vessel.

Previous researchers (Grady *et al*., 1989; Smets *et al*., 1996) attempted to overcome the above disadvantages. A respirometer is instead operated on a batch mode to obtain the on-line and real-time measurement of oxygen uptake data with good reliability. Based on the transient oxygen uptake data, a nonlinear regression method was used to determine the parameters via a grid-searching algorithm for minimizing the sum of squared errors (SSE) between the predicted and experimental oxygen uptake data. The grid-searching algorithm oftentimes is limited to a local SSE instead of the global one. The convergence of the algorithm is affected by the initial conditions of system variables, such as the initial substrate to biomass concentration ratio (S_o/X_o) and S_o/K_s. Wang (1988) suggested an S_o/X_o of greater than 20 for the assurance of the convergence. Smets *et al*. (1996) concluded that an S_o/K_s of greater than 10 is necessary for better convergence. However, reasons for these criteria were not reported and remain to be investigated. Moreover, the appropriate values of the ratios for the convergence may be related to the kinetic parameters, which depend on system characteristics, relating substrate and biomass types (Sperandio and Etienne, 2000).

Wu *et al.* (2001) proposed the separating point (SP) moving algorithm for the determination of kinetics parameters for global minimization. The technique of dimensional analysis can be used to simplify the system parameters and variables into several dimensionless groups so that parameter estimation is less subject to system characteristics. This study aims to use the technique of dimensional analysis incorporated with the SP-moving algorithm so that a set of absolute criteria can be established and used for the experimental design to obtain the more reliable kinetic parameters.

Mathematical deviation

The microbial system

The microbial system considered in this study is toward the concept of potential or intrinsic study, i.e. the test should be conducted under conditions without inhibition or limitation. The reaction vessel (normally 300–1,000 mL) used for respirometric operation is the ideal system for the potential study. The vessel is normally a closed system and is supplied with pure oxygen. This will avoid vapor loss and maintain the constant volume required for operation at a constant SRT. A heavy-duty magnetic bar is operated at high speeds (500–1,000 rpm) so that sufficient mixing can be achieved to avoid the limitation in oxygen transfer. The testing cultures should be properly enriched with sufficient nutrients, buffers, and trace elements. Seed cultures should be acclimated to the testing substrate and operating conditions prior to transferring into the test vessel for kinetic study. Also a proper amount of seed culture should be used to avoid excessive or inadequate seeding. The system is normally operated under semi-continuous conditions with a cyclic batch feed to obtain repeatable data.

Dimensional analysis

Based on the microbial system described above, the governing equations and boundary conditions were expressed in Table 1 of Eqs (1)–(6). As shown in Table 1, the governing equations and boundary conditions contain: one independent variable of time (t); three dependent variables of substrate (S), biomass (X), and accumulated oxygen uptake (O_u); four kinetic parameters of maximal specific growth rate (μ_m), half-saturation constant (K_s), gross growth yield (Y_g), and decay coefficient (k_d); and three operating variables of the feeding concentration of substrate (S_f), sludge retention time (θ_c), and wasting frequency (f_w). Since there are so many parameters related to the considered microbial system, it is difficult to explore the effect of each parameter on system performance. The widely used technique of dimensional analysis was proposed for the system to simplify the governing equations and boundary conditions by aggregating some variables into a one dimensionless group (Himmelblau and Bischoff, 1968). The derivation of the dimensional analysis is shown in Table 1. Table 1 shows that the governing Eqs of (1), (2), and (4) and boundary conditions of (5) and (6) can be grouped into the dimensionless forms of Eqs (16)–(18), and (5a)–(5b), respectively. And, all the system parameters of the kinetic and operating ones can be aggregated into six dimensionless groups: μ_m/f_w, k_d/f_w, Y_g, S_o/K_s, K_s/S_o, and $1/(f_w\,\theta_c - 1)$.

Sensitivity analysis

Based on the six dimensionless groups, sensitivity analysis can be performed for the system to determine the important variables affecting the estimation of kinetic parameters. To solve for the kinetic parameters, Wu *et al.* (2001) developed two analytical equations based on the respirometric oxygen uptake data describing the plot with oxygen uptake rate (OUR) vs. accumulated oxygen uptake (O_u). The plot can be mathematically characterized by two distinct phases, one comprising a hyperbolic function representing exogenous respiration

Table 1 Dimensional analysis of governing equations and their initial and final conditions for the kinetic study of the respirometric system under semi-continuous operation

Derivation	Equations or definitions
Equation of continuity	(1) $dX/dt = \mu_g X - k_d X$
Substrate utilization	(2) $dS/dt = -\mu_g X/Y_g$
Monod kinetics	(3) $\mu_g = \mu_m S/(K_s + S)$
BOD balance equation	(4) $dO_u/dt = -(dS/dt + dX/dt)$
The initial conditions	(5) $O_u = 0$, $S = S_o$, $X = X_o$, at $t = 0$
The final conditions	(6) $O_u = O_{u1}$, $S = 0$, $X = X_1$, at $t = t_1$
Relation of V_f and f_w	(7) $V/V_f = f_w \theta_c = \theta_c/t_1$
Dimensionless variables	(8) $X^* = X/X_o$
	(9) $S^* = S/S_o$
	(10) $O_u^* = O_u/O_{u1}$
	(11) $t^* = t/t_1$
Mass balance derived from (5), (6), and (4) respectively	(12) $X_o V = X_1 (V - V_f) + 0 \times V_f$
	(13) $S_o V = 0 (V - V_f) + S_f V_f$
	(14) $O_{u1} - 0 = -[(0 - S_o) + (X_1 - X_o)]$
Derived from (7)	(15) $t_1 = 1/f_w$
Rewrite (12)–(13) with (7) for V_f/V	(12a) $X_o = X_1 [1 - 1/(f_w \theta_c)]$
	(13a) $S_o = S_f/(f_w \theta_c)$
Rewrite (14) with (12a) for X_1	(14a) $O_{u1} = S_o - X_o/(f_w \theta_c - 1)$
Rewrite (8)	(8a) $X = X^* X_o$
Rewrite (9)	(9a) $S = S^* S_o$
Rewrite (10) with (14a)	(10a) $O_u = O_u^* O_{u1} = O_u^* [S_o - X_o/(f_w \theta_c - 1)]$
Rewrite (11) with (15)	(11a) $t = t^* / f_w$
(3) into (1) with (8a), (9a), (11a)	(16) $dX^*/dt^* = [(\mu_m/f_w) S^*/(K_s/S_o + S^*) - k_d/f_w] X^*$
	(17) $-dS^*/dt^* = \{[(\mu_m/f_w) S^* / (K_s/S_o + S^*)]/(Y_g S_o/X_o)\}X^*$
(3) into (2) with (8a), (9a), (11a)	(18) $dO_u^*/dt^* = -(dS^*/dt^*)/\{1 - 1/[(S_o/X_o)(f_w \theta_c - 1)]\} - (dX^*/dt^*)/[(S_o/X_o) - 1/(f_w \theta_c - 1)]$
(8a)–(11a) into (4)	
(8a)–(11a) into (5)	(5a) $O_u^* = 0$, $S^* = 1$, $X^* = 1$, at $t^* = 0$
(8a)–(11a) into (6) with (12a) and (14a)	(6a) $O_u^* = 1$, $S^* = 0$, $X^* = f_w (_c/(f_w \theta_c - 1) = 1 + 1/(f_w \theta_c - 1)$, at $t^* = 1$

and another a linear function representing endogenous respiration. To estimate the kinetic parameters, the hyperbolic function and the linear function are simultaneously solved, the first one by a multiple linear regression method and the second one by a simple linear regression method. By moving the separation point (SP) between two phases, the best SP can be determined with the optimal fitting between the given and simulated OUR vs. O_u curves.

An average of the absolute relative error (ARE) between the predicted and initially assumed values of the kinetic parameters can be calculated as a performance indicator of the sensitivity analysis. Figure 1 explains the algorithm of the sensitivity analysis for this study. As shown in Figure 1, a set of 4 system parameters and 3 operating variables with appropriate values was first obtained from the literature (Metcalf and Eddy, 1991) to generate OUR and O_u data. The SP-moving algorithm developed by Wu *et al.* (2001) was used to estimate the kinetic parameters. For each given set of system parameters and variables, the value of $\mathrm{ARE} = (|\mu_m^e - \mu_m|/\mu_m + |Y_g^e - Y_g|/Y_g + |K_s^e - K_s|/K_s + |k_d^e - k_d|/k_d)/4 \times 100\%$ was calculated, where the superscript of e stands for estimated values. The six dimensionless groups: μ_m/f_w, k_d/f_w, Y_g, S_o/K_s, K_s/S_o, and $1/(f_w \theta_c - 1)$ were then calculated. By using 3 values for each parameter and variable within a reasonable range, a total number of 3^7 (2187) sensitivity analyses were performed to investigate the relative importance of the six dimensionless groups for this study. In which, maximal specific growth rate (μ_m) of 3.6 1/d, half-saturation constant (K_s) of 70 mg/L BOD, gross growth yield (Y_g) of 70 mg/L BOD, decay coefficient (k_d) 0.06 1/d, substrate feeding concentration (S_f) of 2,000 mg/L BOD, sludge

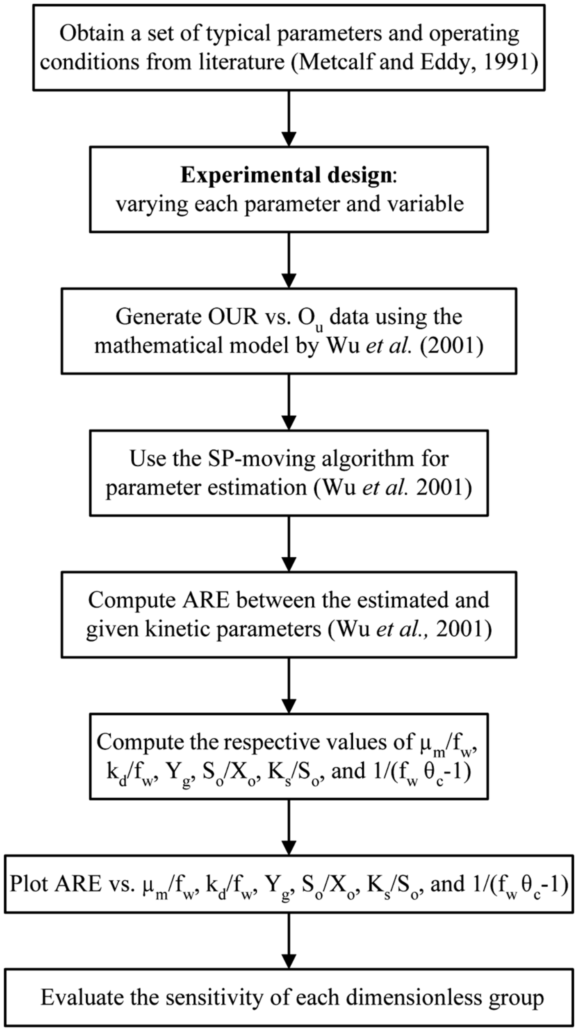

Figure 1 The proposed algorithm of sensitivity analysis for kinetic study of this study

retention time (θ_c) of 10 d, and θ_c-based wasting frequency (f_w θ_c) of 4 are used, and each parameter is manipulated by –25% – +25%.

Results and discussions

The system variables were used to estimate the four kinetic parameters. For each set of variables, an average of the absolute relative error (ARE) between the estimated and initially assumed values of the kinetic parameters was calculated. Six plots were generated using the calculated ARE vs. μ_m/f_w, k_d/f_w, Y_g, S_o/K_s, K_s/S_o, and $1/(f_w - 1)$, respectively. As shown in Figures 2A and 2B, it can be seen that both plots have no significant effect on ARE. Since Figures 2A and 2B are related to only one operating variable f_w, it is indicated that f_w itself is not a sufficient factor for kinetic study. As shown in Figure 2C, Y_g is an important variable for ARE since decreasing Y_g decreases ARE significantly. As shown in Figures 2D and 2E, it can be seen that both plots converge to a relatively small ARE. At a corresponding ARE limit, a value of S_o/X_o and S_o/K_s was determined from each plot so that a laboratory study can be better designed to determine the kinetic parameters. It can be concluded from Figure 2D and 2E that values of $S_o/X_o > 1.3$ and $K_s/S_o < 0.1$ are the appropriate testing criteria for

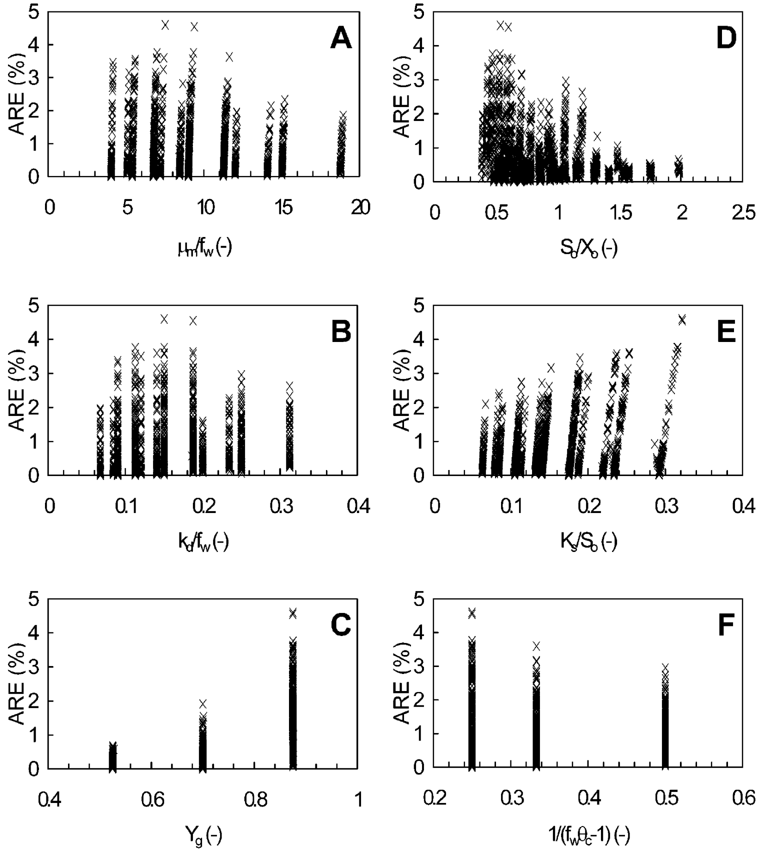

Figure 2 Results of sensitivity analysis of the six dimensionless groups, showing irregular trend for μ_m/f_w and k_d/f_w, and regular trend for Y_g, S_o/X_o, K_s/S_o, and $1/(f_w\,\theta_c - 1)$.

kinetic study. The S_o/X_o value of 1.3 is different from 20 reported by Wang (1988). The K_s/S_o value of 0.1 agrees with the values of S_o/K_s of 10 reported by Smets *et al.* (1996). As shown in Figure 2F, increasing $1/(f_w\,\theta_c - 1)$ can also decrease ARE. Comparing Figure 2F with Figures 2A and 2B also suggests that $f_w\,\theta_c$ is a more important factor than f_w for kinetic study since increasing $1/(f_w\,\theta_c - 1)$ equals decreasing $f_w\,\theta_c$.

Comparing Figures 2D and 2E, it can be found that S_o/X_o is a more important factor than K_s/S_o. This is probably due to that the effect of S_o/X_o for a semi-continuous operation mode is directly related to Y_g. It can be seen that decreasing Y_g will decrease ARE as shown in Figure 2C; however, decreasing Y_g can also decrease X_o during semi-continuous operation. Therefore, lower Y_g will make S_o/X_o larger, and converge ARE.

Concluding the results from Figures 2A–2F, Y_g is the most important factor parameter estimation, but it is not an operating variable which can be manipulated. Otherwise, S_o/X_o is the most important one, however its effect is mostly caused by Y_g. Therefore K_s/S_o is actually the most important operating factor for kinetic study. Moreover, $f_w\,\theta_c$ is also a more important one than f_w, as indicated by comparing Figure 2F with Figures 2A and 2B.

Conclusions

Based on the results of this study, the following conclusions can be drawn.

1. A novel dimensional analysis was proposed for this study to identify the six dimensionless groups: μ_m/f_w, k_d/f_w, Y_g, S_o/K_s, K_s/S_o, and $1/(f_w\,\theta_c - 1)$ so that better criteria for testing conditions can be developed for more reliable parameter estimation in kinetics studies.

2. Comparing Figures 2A–2F, sensitivity analysis reveals that the criterion for Y_g is the most sensitive dimensionless group to ARE. However, the gross growth yield is only intuitive to the wastewater and microorganisms of the system, but no operating variable can be manipulated. It can be concluded that S_o/X_o is more sensitive than K_s/S_o. However, the effect of S_o/X_o is amplified by Y_g, since decreasing Y_g (less synthesis) will decrease X_o and consequently increase S_o/X_o during the semi-continuous operation. Moreover, $1/(f_w\,\theta_c - 1)$ or $f_w\,\theta_c$ is more sensitive than μ_m/f_w and k_d/f_w.
3. A critical minimum value of 1.3 can be determined for S_o/X_o from this study, disregarding the type of substrate and biomass. A maximum value of 0.1 for K_s/S_o was suggested to be appropriate from this study. In addition, a smaller value of $f_w\,\theta_c$ gives a better estimate of the kinetic parameters.

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