OXYGEN SAG EQUATION FOR HALF ORDER BOD KINETICS*

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ABSTRACT

A dissolved oxygen sag equation for a stream is developed in which the biochemical oxygen demand is described as a half order reaction rather than a first order reaction as in the classical Streeter-Phelps equation. The dissolved oxygen equation using half order BOD kinetics is most applicable to rapidly degrading industrial wastes containing glucose and glutamic acid. The time at which the maximum dissolved oxygen deficit occurs is predicted in this model. The dissolved oxygen sag equation is developed for the case in which sedimentation of BOD occurs. However, if both sedimentation and benthic demand occur, a complete analytical solution does not appear possible.

INTRODUCTION

The Streeter-Phelps equation for the dissolved oxygen in a stream has been widely studied and applied in environmental engineering. The equation relates the oxygen demand exerted upon a stream by a biodegradable waste to the natural recovery process for a stream through reaeration. First developed by Streeter and Phelps [1] during their studies of pollution on the Ohio River, the equation is derived from the relationship

$$\frac{dD}{dt} = k_1 L - k_2 D \tag{1}$$

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where

    D = dissolved oxygen deficit, C_s - C, mg/L

    C_s = saturation value for dissolved oxygen, mg/L

    C = dissolved oxygen concentration in the stream, mg/L

    k_1 = biochemical oxygen demand deoxygenation rate constant, day^{-1}

    L = biochemical oxygen demand yet to be satisfied, mg/L, also L means liter

    k_2 = reaeration rate constant, day^{-1}

The biochemical oxygen demand is treated as a first order reaction so that

$$\frac{dL}{dt} = -k_1 L \tag{2}$$

which integrates to $L = L_0 \exp(-k_1 t)$, where L_0 is the ultimate carbonaceous biochemical oxygen demand and k_1 is the reaction rate constant, assumed to be equal to the deoxygenation rate constant. Combining Equations (1) and (2) and integrating leads to the classical Streeter-Phelps equation

$$D = \frac{k_1 L_0}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] + D_0 \exp(-k_2 t) \tag{3}$$

where D_0 is the dissolved oxygen deficit at time zero.

A large number of variations of the basic Streeter-Phelps differential equation have been developed to extend its range of applicability. These variations include the addition of terms to account for the effect of benthic deposits, photosynthesis, sedimentation, and temperature [2, 3]. Some attention has been given to the form of the kinetic equation for BOD. For example, Thomas [4] and Young and Clark [5] proposed a second order BOD reaction equation. Braun and Berthouex [6] proposed a Mechalis-Menten expression for the BOD kinetics. Apparently, the half order BOD kinetic expression has not been incorporated into a dissolved oxygen sag equation. Reining [7] presented data on BOD decay for various mixtures of glucose and glutamic acid. Analysis of his data showed it was best described by a half order kinetic model. Sutherland [8] and Sutherland et al. [9] reported that a sugarcane factory wash water containing glucose was readily biodegradable but these authors did not develop a dissolved oxygen sag equation.

PURPOSE

The purpose of this article is to develop an oxygen sag equation for a stream in which a half order relationship describes the oxygen demand kinetics of the waste. The mathematical description will retain the basic form of Equation (1), but will change the form of Equation (2) so that a half order BOD equation can be used [10]. The mathematics of the half order BOD equation will be reviewed first; then the equation which incorporates this type of BOD demand into the dissolved

oxygen budget of a stream will be developed. Finally, the consequences of using the revised equation will be explored through examples.

HALF ORDER BOD EQUATION

Derivation

The half order BOD equation is developed from the premise that the reaction rate is given by the expression

$$\frac{dL}{dt} = -k_{1/2} L^{1/2} - k_3 L + L_a \tag{4}$$

where the terms are as previously defined, except that $k_{1/2}$ is the half order rate constant $(mg/L)^{1/2}/day$; k_3 is the sedimentation rate constant, day^{-1}; and L_a is the benthic deposits addition to BOD, $mg/L/day$. When $k_3 = 0$ and $L_a = 0$, Equation (4) integrates to

$$L = (L_0^{1/2} - k_{1/2} t/2)^2 \tag{5}$$

When $t_1 = 2L_0 1/2/k_{1/2}$, there is no remaining organic material to degrade so that $L = 0$ for $t > t_1$, otherwise Equation (5) would show L increasing for $t > t_1$. When $k_3 \neq 0$ but $L_a = 0$, Equation (4) integrates to

$$L = \left[L_0^{1/2} \exp\left(-\frac{k_3 t}{2}\right) - \frac{k_{1/2}}{k_3}\left(1 - \exp\left(-\frac{k_3 t}{2}\right)\right)\right]^2 \tag{6}$$

When $t_1 = \dfrac{2}{k_3} \ln\left(\dfrac{L_0^{1/2} k_3 + k_{1/2}}{k_{1/2}}\right)$ the BOD is zero and one should specify $L = 0$ for $t > t_1$.

When $k_{1/2}$, k_3 and L_a are all present, Equation (4) integrates to

$$\ln \left\{ \frac{\left(L + \dfrac{k_{1/2}}{k_3} L^{1/2} - \dfrac{L_a}{k_3}\right)}{\left(L_0 + \dfrac{k_{1/2}}{k_3} L_0^{1/2} - \dfrac{L_a}{k_3}\right)} \left[\frac{(L_0^{1/2} - \beta)(L^{1/2} + \alpha)}{(L^{1/2} - \beta)(L_0^{1/2} + \alpha)}\right]^{\frac{k_{1/2}}{k_{1/2}^2} + 4L_a k_3} \right\} = -k_3 t \tag{7}$$

where

$$\alpha = \frac{1}{2}\left(\frac{k_{1/2}}{k_3} + \sqrt{\left(\frac{k_{1/2}}{k_3}\right)^2 + \frac{4L_a}{k_3}}\right) \tag{8}$$

and

$$\beta = \frac{1}{2}\left(-\frac{k_{1/2}}{k_3} + \sqrt{\left(\frac{k_{1/2}}{k_3}\right)^2 + \frac{4L_a}{k_3}}\right) \tag{9}$$

$L(t)$ is contained as an implicit function in Equation (7). Examination of Equation (4) shows that when $L_a \neq 0$, the steady state is

$$L^{1/2} = \frac{1}{2}\left\{-\frac{k_{1/2}}{k_3} + \sqrt{\left(\frac{k_{1/2}}{k_3}\right)^2 + \frac{4L_a}{k_3}}\right\}$$ (10)

Determination of Model Parameters

The half order BOD equation lends itself to straight-forward determination of the constants $k_{1/2}$ and L_0 from experimental data, especially when $k_3 = L_a = 0$. The conventional BOD bottle test gives values of the amount of oxygen consumed by a sample as a function time. If y represents the amount of oxygen consumed at any time, the relationship $L_0 - y = L$ can be substituted into Equation (5) to obtain the parabolic equation

$$y = k_{1/2}L_0^{1/2}t - (k_{1/2}\,t/2)^2$$ (11)

which can be rearranged in one of the following linear forms

$$\frac{y}{t} = -\frac{k_{1/2}^2\,t}{4} + k_{1/2}\,L_0^{1/2}$$ (12)

or

$$\frac{y}{t^2} = \frac{k_{1/2}\,L_0^{1/2}}{t} - \frac{k_{1/2}^2}{4}$$ (13)

$$\frac{t}{y} = \frac{k_{1/2}\,t^2}{4L_0^{1/2}\,y} + \frac{1}{k_{1/2}\,L_0^{1/2}}$$ (14)

or

$$\frac{t^2}{y} = \frac{4L_0^{1/2}}{k_{1/2}}\frac{t}{y} - \frac{4}{k_{1/2}^2}$$ (15)

from which the parameters $k_{1/2}$ and L_0 can be determined from the ordinate intercept and slope of the line. Of course, to avoid the problem of predicting unrealistic results, $k_{1/2}$ and L_0 must be positive. Also, Equation (11) would predict a negative oxygen consumption for large times so the restriction that $t \leq 2\,L_0 1/2/k_{1/2}$ is still necessary.

An alternative procedure for determining $k_{1/2}$ and L_0 is to find their values such that the best fit in the least squares sense is obtained using Equation (11) and the measured values of y versus t. This procedure may be advantageous if one were processing large amounts of data, or if the linear forms illustrated in Equations (12)–(15) show bias in the calculated values of $k_{1/2}$ and L_0. A difficulty arises in

the calculations because t_1 is a function of L_0 and $k_{1/2}$, both of which are unknowns. A practical solution is to use all the y vs. t data to calculate $k_{1/2}$ and L_0. Then calculate t_1. Then check to determine whether any data used in the calculation had $t > t_1$. If so, then those data points would be eliminated and revised values of $k_{1/2}$ and L_0 would be calculated and the new t_1 determined. The least squares values of $k_{1/2}$ and L_0 would be calculated by minimizing the square of residual error in the function

$$SRE = \sum_{i=1}^{i=N} [y(t_i) - \hat{y}(t_i)]^2 \tag{16}$$

where $y(t_i)$ is the measured value and $\hat{y}(t_i)$ is predicted from Equation (11).

Reining analyzed the effect of dilution on the BOD kinetics of a 1:1 mixture of glucose and glutamic acid, containing 175 mg/L of each [7]. The above mixture was tested on a manometric apparatus in a series of dilutions so that the sample strength varied from 10 percent of full strength to 100 percent of full strength. Ten replicates for each dilution were measured at daily intervals. Examination of Reining's data shows that the wastes which were 40 percent strength or less follow half order kinetics. Table 1 shows the data from the ten replicate readings for the

Table 1. Daily Dissolved Oxygen Uptake Values in mg/L for 30% Strength Waste for Ten Replications

Replication	Day				
	1	2	3	4	5
1	43.9	58.0	63.6	65.0	65.0
2	41.1	45.2	47.8	47.8	47.8
3	29.5	56.6	58.8	59.4	61.2
4	22.6	57.6	62.9	64.6	65.3
5	13.1	44.7	52.7	57.0	65.8
6	26.5	57.5	66.2	66.2	66.2
7	17.8	47.9	65.0	70.9	82.1
8	24.2	51.7	65.3	65.3	65.3
9	44.9	49.1	57.1	62.4	67.3
10	43.5	58.0	63.1	66.9	74.5
$\bar{y}$	30.71	52.63	60.25	62.55	66.05
σ_y	11.79	5.53	6.09	6.48	8.75
$\bar{y}/t^2$	30.71	13.16	6.69	3.91	2.64
$\sigma_{(y/t^2)}^2$	11.79	1.38	0.68	0.41	0.35

30 percent of full strength samples. The table has been augmented so Equation (13) can be used to determine the kinetic parameters $k_{1/2}$ and L_0 from Figure 1.

Examination of Figure 1 shows the intercept on the vertical axis is −5.0. From Equation (13), the intercept is − $k^2_{1/2}/4$, so $k_{1/2}$ = 4.472 $mg^{1/2}/L^{1/2}$-d. The slope is 35.94. Equation (13) shows the slope is $k_{1/2}L_0^{1/2}$, so L_0 = 64.59 mg/L. Examination of the data in Table 1 shows that by day four replicates one, two, six, and eight ceased to consume any more dissolved oxygen. Replicates two, six, and eight ceased to consume dissolved oxygen by day three. Thus, if a sample is expected to follow half order kinetics, then it is important to collect data earlier rather than later in the test period. In other words, data collected early in the test period will have $t < t_1$. For Figure 1, $t_1 = 2 L_0^{1/2}/k_{1/2}$ = 3.59 day. The line of best fit in Figure 1 would undergo a negligible change if the data for days four and five were eliminated.

OXYGEN SAG EQUATION FOR HALF ORDER BOD KINETICS

The appropriate differential equation describing the dissolved oxygen concentration in a stream is obtained from the conservation of mass principle applied to dissolved oxygen. The mass balance relationship results in
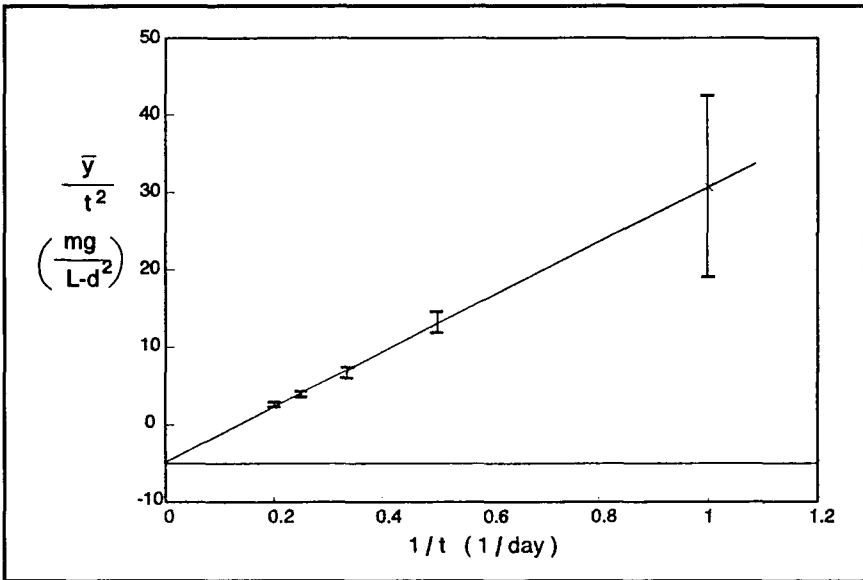

Figure 1. Thirty percent strength oxygen uptake data for a 1:1 mixture of glucose and glutamic acid. Plotted points are the mean of ten replications. Bars are at ± one standard deviation.

$$\frac{dC}{dt} = k_2(C_s - C) - k_{1/2} L^{1/2} \tag{17}$$

We will look at three cases for the dissolved oxygen concentration: (a) $k_3 = L_a = 0$, (b) $k_3 \neq 0$, $L_a = 0$, and (c) $k_3 \neq 0$ and $L_a \neq 0$. For the first case, we substitute Equation (5) into Equation (17) to obtain

$$\frac{dC}{dt} = k_2(C_s - C) - k_{1/2} (L_0^{1/2} - k_{1/2} t/2) \tag{18}$$

for $t \leq 2L_0^{1/2}/k_{1/2}$. When t is larger than this value, there is no oxygen demand from the waste and Equation (17) becomes

$$\frac{dC}{dt} = k_2(C_s - C) \tag{19}$$

As the solution to Equation (18) is not readily available in stream pollution books [3, 11, 12], the derivation will be presented in some detail below.

Equation (18) has the integrating factor $\exp(k_2 t)$. After integrating, the following expression is obtained

$$C = C_0 \exp(- k_2 t) + [(k_2 C_s - k_{1/2} L_0^{1/2})/k_2] (1 - \exp(-k_2 t))$$
$$+ (k_{1/2}^2/2 k_2) ((t - 1/k_2) + (1/k_2) \exp(-k_2 t)) \tag{20}$$

where C_0 is the dissolved oxygen concentration when $t = 0$. This expression for the dissolved oxygen concentration is applicable until $t_1 = 2 L_0^{1/2}/k_{1/2}$. For $t > t_1$, Equation (19) integrates to

$$C (t) = C (t_1) \exp (- k_2(t - t_1)) + C_s (1 - \exp (- k_2 (t - t_1))) \tag{21}$$

Equations (20) and (21) are the forms of the dissolved oxygen expression for BOD following half order kinetics which are most convenient for application. If one prefers to work in terms of the dissolved oxygen deficit, Equation (20) may be rearranged to have the form

$$D = D_0 \exp (-k_2 t) + (k_{1/2}^2/k_2) (L_0^{1/2} - k_{1/2}/(2k_2)) (1 - \exp (-k_2 t))$$
$$- (k_{1/2}^2 t)/(2k_2) \tag{22}$$

and Equation (21) becomes

$$D (t) = D_1 \exp (- k_2 (t - t_1)) \tag{23}$$

where D_1 is the value $C_s - C (t_1)$. Equations (22) and (23) are analogous to Equation (3), except they are applicable for a half order BOD demand.

For case (b), $k_3 \neq 0$ but $L_a = 0$. Equation (6) gives the BOD concentration remaining as a function of time. Combining Equations (6) and (17) yields

$$\frac{dC}{dt} = k_2(C_s - C) - k_{1/2} \left[L_0^{1/2} \exp \left(-\frac{k_3 t}{2} \right) - \frac{k_{1/2}}{k_3} \left(1 - \exp \left(-\frac{k_3 t}{2} \right) \right) \right] \tag{24}$$

Again, the integrating factor is exp $k_2 t$. After applying the integrating factor and integrating, one obtains

$$C = C_0 \exp(-k_2 t) + \left(C_s + \frac{k_{1/2}^2}{k_2 k_3} \right) [1 - \exp(-k_2 t)]$$

$$- \frac{k_{1/2} \left(L_0^{1/2} + \frac{k_{1/2}}{k_3} \right)}{k_2 - \frac{k_3}{2}} \left[\exp\left(-\frac{k_3 t}{2} \right) - \exp(-k_2 t) \right] \tag{25}$$

This equation is applicable for $t \le t_1$ where t_1 was shown previously to be

$$t_1 = \frac{2}{k_3} \ln \left(\frac{L_0^{1/2} k_3 + k_{1/2}}{k_{1/2}} \right) \tag{26}$$

For $t > t_1$, Equation (19) is applicable and the dissolved oxygen is given by Equation (21) (using Equations (25) and (26) to compute $C(t_1)$).

For case (c), $k_3 \ne 0$ and $L_a \ne 0$. Equation (7) gives the BOD concentration remaining as a function of time, but the BOD concentration remaining, $L(t)$, is an implicit function of time. One cannot solve Equation (7) explicitly for $L(t)$. Thus, the dissolved oxygen differential equation, Equation (17), cannot be solved analytically and one would have to apply a numerical solution, which is beyond the scope of this investigation.

MINIMUM DISSOLVED OXYGEN

The time when the minimum dissolved oxygen concentration occurs, t_c, is of obvious interest. When $k_3 = L_a = 0$, it may be calculated from Equation (22) by noting that at the minimum point $dD/dt = 0$. Carrying out the calculation produces the result

$$t_c = - (1/k_2) \ln \left[\frac{k_{1/2}^2}{k_{1/2}^2 + 2k_{1/2} k_2 \sqrt{L_0} - 2k_2^2 (C_s - C_0)} \right] \tag{27}$$

The critical value can be solved for explicitly. If $t_c > t_1$, then the minimum dissolved oxygen concentration would occur when $t_c = 0$ or when $t_c = t_1$.

When Equation (25) is applicable in describing the dissolved oxygen concentration, it may be differentiated and the derivative set equal to zero to find the time at which the minimum concentration occurs. The critical time at which the minimum occurs is

$$t_c = \frac{1}{k_2 - \frac{k_3}{2}} \ln \left\{ \frac{k_2(k_3 - 2k_2)\left[C_s - C_0 + \frac{k_{1/2}}{k_2 k_3} + \frac{2k_{1/2}\left(L_0^{1/2} + \frac{k_{1/2}}{k_3}\right)}{2k_2 - k_3}\right]}{k_3 k_{1/2}\left(L_0^{1/2} + \frac{k_{1/2}}{k_3}\right)} \right\} \qquad (28)$$

If the calculated $t_c > t_1$, where t_1 is obtained from Equation (26), then the minimum dissolved oxygen concentration would occur when $t_c = 0$ or when $t_c = t_1$.

APPLICATION OF THE OXYGEN SAG EQUATION

The use of the oxygen sag equation for a half order BOD demand is illustrated for the following situation. A waste having a half order reaction rate coefficient of 3.5 $(mg/L)^{1/2}$/day is discharged to a stream. The streamflow is such that after mixing, the ultimate first stage BOD is 15 mg/L and the reaction rate coefficient remains unchanged. The dissolved oxygen saturation value is 10 mg/L and the initial dissolved oxygen value is 9 mg/L. The reaeration rate is 0.6/day. The sedimentation rate is negligible and there is no benthic oxygen demand. Using these data as input to Equations (20) and (21) produces the results tabulated in Table 2. The time for which $L = 0$ is $t_1 = 2 L_0 1/2/k_{1/2} = 2.213$ day. The minimum dissolved oxygen concentration calculated by Equation (27) occurs when $t_c = 1.337$ days.

Table 2. Dissolved Oxygen
Concentrations for
Half Order BOD Kinetics

t Days	C mg/L	Calculated by Equation
0	9.00	(20)
1	1.790	(20)
1.337	1.351	(20)
2	2.438	(20)
2.213	3.218	(20)
3	5.771	(21)
4	7.679	(21)
5	8.726	(21)
6	9.301	(21)
7	9.616	(21)

CONCLUSIONS

A dissolved oxygen equation for a stream has been developed in which the biochemical oxygen demand is expressed as a half order kinetic reaction. The half order reaction kinetics permit the BOD to decay to zero in a finite time. This phenomenon is not observed with first order kinetic models. When sedimentation and benthic demand occur, one can obtain a relationship between BOD and time, however, the relationship gives the BOD only implicitly as a function of time.

The dissolved oxygen equation based upon half order kinetics is readily solved when benthic demand is absent. When benthic demand is present, an analytical solution appears intractable and a numerical solution may be appropriate. The location of the minimum dissolved oxygen concentration can be calculated readily except when benthic demand is present. Half order kinetics are appropriate for glucose and glutamic acid wastes. It is speculative whether dilute concentrations of sugar factor wastewater follow half order kinetics as they break down in a receiving water.

NOMENCLATURE

C = dissolved oxygen concentration in the stream, mg/L
C_s = saturation value of dissolved oxygen, mg/L
D = dissolved oxygen deficit, $(C_s - C)$, mg/L
D_0 = dissolved oxygen deficit at time zero
k_1 = biochemical oxygen demand rate constant taken as equal to the deoxy genation rate constant, day^{-1}
k_2 = reaeration rate constant, day^{-1}
$k_{1/2}$ = half order biochemical oxygen demand rate constant, $(mg/L)^{1/2}/day$
L = biochemical oxygen demand yet to be satisfied, mg/L
L_0 = ultimate biochemical oxygen demand, mg/L
t = time, day
t_1 = time for which $L = 0$, day
t_c = time at which the minimum dissolved oxygen concentration occurs, day
y = amount of oxygen consumed at any time $(L_0 - L)$, mg/L

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