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Modeling of nitrification in the BOD test

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ABSTRACT

Nitrogen compounds present in water exert an oxygen demand when assimilated by autotrophic bacteria. Nitrification is slower than **BOD** exertion by the carbonaceous material and may take several days until completion. Nitrification is particularly important when wastes introduced into water are already seeded with nitrifying bacteria, and it is affected most by the organism growth rate. Two models are developed to describe the nitrogenous oxygen demand based on microbial growth. The first model is a modification of the Monod model in which growth and decay phases are treated separately. The second is a nonhomogeneous birth and death model with constant birth rate and death rate linearly increasing with time. The model parameters were determined by nonlinear least squares schemes for six sets of nitrogenous BOD data which corresponded to activated sludge effluent, river water mixed with treated effluent, two trickling filter effluent samples, raw sewage, and facultative pond effluent. Both models were observed to represent the BOD exertion due to nitrification reasonably well.

NOMENCLATURE

The following symbols are used in this paper:

$a_1, \ldots, a_5$ = coefficients in the approximation for error functions;
BOD = biochemical oxygen demand;
C = ratio between oxygen demand and total bacterial life;
$c_1, \ldots, c_5$ = linearized least squares parameters;
D_1 = denominator in Eqns (19);
D_2 = denominator in Eqns (25);
erf = error function;
F = inverse function of an F distribution;
$f_1, \ldots, f_4$ = least squares variables;
g = difference between normal equations;
i = summation index;
j = iteration number;
K_a, K_b = rate constants for nitrogenous BOD exertion;
K_s = saturation coefficient;
L_0 = ultimate first stage BOD;
L_a, L_b = limiting values of nitrogenous BOD;
m = number of data points for $t < t_0$;

N = bacterial population at time t;
N_0 = initial bacterial population;
n = total number of data points;
p = number of least squares parameters;
q = confidence level;
r = correlation coefficient;
S = error sum of squares;
S_0 = initial substrate concentration;
$S_1, \ldots, S_4$ = least squares sums;
sq = confidence contour;
S_t = substrate concentration at time t;
t = time;
t_0 = critical time;
u = dummy variable;
$X = y/\alpha$;
X_0 = initial microorganism concentration;
Y = growth yield coefficient;
y = BOD exerted;
$\bar{y}$ = mean value of BOD;
$\hat{y}$ = estimated value of BOD;
z = argument of error function;
α = half of ultimate second stage BOD;
$\hat{\alpha}$ = least squares estimate of α;
Δt = time increment;
$\Delta\mu$ = increment in μ;
δK_a = correction in K_a;
δK_b = correction in K_b;
ϵ = absolute error;
λ = birth rate;
μ = death rate per unit time;
$\hat{\mu}$ = least squares estimate of μ; and
μ_m = maximum specific growth rate.

INTRODUCTION

Nitrogenous material present in raw sewage and partially treated wastewaters may be oxidized by certain autotrophic bacteria. This process is termed nitrification and its contribution to the oxygen demand in the BOD test is commonly called second-stage BOD. In the classical BOD tests, BOD exertion by the carbonaceous material predominates at small times and in general exertion of the nitrogenous biochemical oxygen demand is not noted in the BOD test at times less than five to eight days. However, if samples are taken from the effluents of wastewater treatment plants already seeded with nitrifying bacteria, nitrogenous BOD exertion can start immediately. In fact, nitrification occurs in most effluents that have undergone partial oxidation of the waste components, and it should be considered as a part of the total BOD of the waste on the dissolved oxygen balance of water bodies. Since the exertion of carbonaceous and nitrogenous BOD are separate processes, they should be reported separately.

The nitrogen balance in water bodies is complex and transformation of nitrogen compounds may be caused by the assimilation of ammonium and nitrate by both autotrophic and heterotrophic microorganisms, reduction of nitrate and nitrite by denitrifying bacteria, fixation of atmospheric nitrogen by algae and bacteria, production of ammonia by deamination of cell organic nitrogen and oxidation of ammonia and nitrite by nitrifying bacteria. However, it is now well established that nitrification by two species of autotrophic bacteria, *Nitrosomonas* and *Nitrobacter*, is the major factor to be expected in rivers (Curtis *et al.* 1975). Nitrification is affected by the population of these organisms and its growth rate that in turn depends on inorganic substrate concentration, temperature, pH, inhibitory and toxic materials, and dissolved oxygen concentration (Stenstorm & Poduska 1980; Painter & Loveless 1983). In addition, dilution of samples in the standard BOD test decreases the influence of inhibitory substances. A nitrification model incorporating all these factors would be considerably involved. The objective of this study is to discuss two simplified bacterial growth models that can describe the nitrification process in the BOD test.

MODELS FOR NITRIFICATION

In the development of models based on microbial growth it is reasonable to assume that the rate of bacterial growth is proportional to the concentration of the existing population and that a constant fraction of the substrate removed is converted to new cell material at a constant rate. If we further assume that the effect of limiting substrate or nutrient on growth rate can be defined by the well known Monod model, the relationship between substrate concentration and time can be expressed as

$$\mu_m t = \frac{K_s}{(X_0/Y + S_0)} \ln\left(\frac{S_0}{S_t}\right) + \frac{(X_0/Y + S_0 + K_s)}{(S_0 + X_0/Y)} \ln\left(1 + \frac{(S_0 - S_t)}{X_0/Y}\right) \qquad (1)$$

in which μ_m = maximum specific growth rate; K_s = saturation coefficient; X_0 = initial microorganism concentration; S_0 = initial substrate concentration; Y = growth yield coefficient; and S_t = substrate concentration at time t (Knowles *et al.* 1965).

Using conventional notation for BOD and lumping constants together, Eqn. 1 can be rewritten to give the relationship between dissolved oxygen consumed and time as

$$t = -\frac{1}{K_b} \ln\left(1 - \frac{y}{L_b}\right) + \frac{1}{K_a} \ln\left(1 + \frac{y}{L_a}\right) \qquad (2)$$

in which

$$K_a = \frac{\mu_m(S_0 + X_0/Y)}{X_0/Y + S_0 + K_s};$$

$$K_b = \frac{\mu_m(X_0/Y + S_0)}{K_s};$$

$$L_a = X_0/Y;$$

$$L_b = S_0;$$

$$y = S_0 - S_t.$$

In Eqn. 2, y can be conveniently referred to as the second stage BOD, K_a and K_b as rate constants, L_a as the initial concentration of nitrifying biomass expressed in terms of the amount of substrate needed to form it, and L_b as the initial substrate concentration.

Recent studies have shown that for very large concentrations of nitrogen compounds, the specific utilization rate continuously decreases with increasing substrate concentration, and the rate of substrate utilization cannot be accurately described using the Monod model (Rozich & Castens 1986; Gee *et al.* 1990). However, for concentrations generally observed in receiving waters, Eqns. 1 or 2 can be used to describe the concentration of ammonia nitrogen or dissolved oxygen in rivers. Some of the parameters can be determined by laboratory analyses, and others can be obtained by curve fitting techniques which require extensive trial-and-error computations (Knowles *et al.* 1965). It is desirable, however, to determine the model parameters K_a, K_b, L_a, and L_b of Eqn. 2 from the BOD test data on t and y. For this purpose, several nonlinear least squares schemes and commercially available regression programs were tested by the author. In all the least squares methods tried, it was necessary to make initial estimates for L_a and L_b. Because of the functional form of Eqn. 2, the iterative schemes almost always diverged. Divergence occurred even if the logarithms in Eqn. 2 were approximated by finite series.

For large concentrations of microorganisms, the second term on the right-hand side of Eqn. 1 can be ignored and the oxygen demand until time t can be written as

$$y = L_b[1 - e^{-K_b t}] \tag{3}$$

Clearly Eqn. 3 describes the exertion of oxygen demand as the system follows first-order kinetics. The parameter L_b represents the ultimate oxygen demand. Conventionally, Eqn. 2 is used to define the first stage BOD due to oxidation of carbonaceous material. In this stage, heterotrophic bacteria multiply very rapidly to reach a maximum population in a short lag time. Oxygen utilization in the lag phase is not considered in the analysis. Although the microorganisms responsible for nitrification multiply much slower than the heterotrophs and the lag phase may continue for several days, Eqn. 3 is frequently used as the basic mathematical model describing the nitrification process (Camara & Randall 1984; Todd & Bedient 1985; Warwick & McDonnel 1985; McCutcheon 1987). Probably because of its simplicity, even probabilistic dissolved oxygen models use Eqn. 3 as the basic model (Dewey 1984; Zielinski 1988). If the nitrifying organisms are considered to be effective only at the end of a lag period, Eqn. 2 can be modified as

$$\begin{aligned} y &= 0 & t &< t_0 \\ &= L_b[1 - e^{-K_b(t-t_0)}] & t &\geqslant t_0 \end{aligned} \tag{4}$$

in which t_0 = the delay time before nitrifying organisms are effective.

For small concentrations of microorganisms, the first term on the right-hand side of Eqn. 2 can be neglected and the oxygen demand for small bacterial populations and large nutrient concentrations can be expressed as

$$y = L_a(e^{K_a t} - 1) \tag{5}$$

The exertion of oxygen demand as the microorganisms grow exponentially is described by Eqn. 5. Here L_a can be considered as a factor relating initial bacterial population and the rate constant to oxygen utilization. Courchaine (1962) assumes that in the initial phases of nitrification, nitrifying bacteria grow exponentially; however, once the maximum population is reached, exponential death phase starts immediately. The growth and death rates are obviously different. The growth phase, or the lag period, will continue up to the critical time t_0. Thus, the exertion of oxygen demand can be described by Eqn. 5 until time t_0, and by Eqn. 3 beyond t_0. After making the coordinate transformation to express the total BOD exertion after t_0, the resulting equations become

$$\begin{aligned} y &= L_a[e^{K_a t} - 1] & t < t_0 \\ &= L_a[e^{K_a t_0} - 1] + L_b[1 - e^{-K_b(t-t_0)}] & t \geqslant t_0 \end{aligned} \tag{6}$$

A schematic representation of the BOD exertion according to Eqn. 6 is shown in Fig. 1. This model will be referred to as the five-parameter second stage BOD. It will be subsequently shown that the five parameters of the model; i.e. L_a, L_b, K_a, K_b and t_0, can be estimated with relative ease.

Although the five-parameter BOD model is a simple mathematical expression, the rate of BOD exertion shows a discontinuity at $t = t_0$. A model suggested earlier (Esen, 1974) avoids this discontinuity and reduces the unknown number of model parameters.

Consider a stochastic death process in which the death rate is constant. The mean value of the bacterial population N at any time is

$$N = N_0 e^{-\mu t} \tag{7}$$

in which N_0 = initial number of microorganisms; and μ = death rate; i.e. the probability of any individual microorganism dying in time Δt is $\mu \Delta t$ (Bailey 1964). If it is assumed that the oxygen demand until time t is proportional to the duration of total bacterial life until that time, the BOD exerted is governed by

$$\frac{dy}{dt} = CN_0 e^{-\mu t} \tag{8}$$

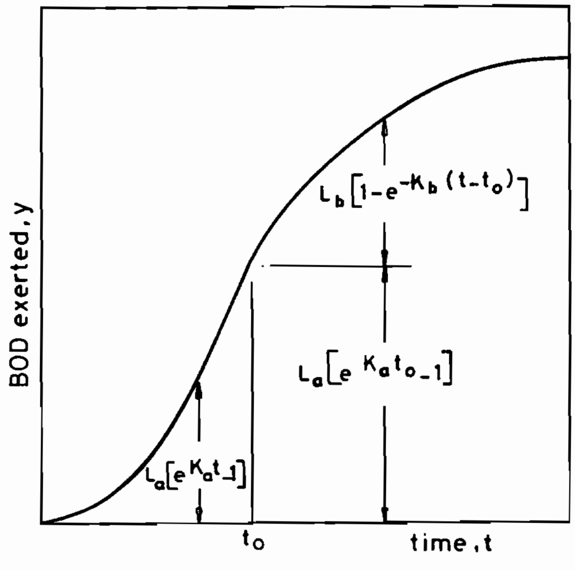

Fig. 1. Nitrogenous BOD exertion (Five-Parameter BOD Model).

Thus,

$$y = \frac{CN_0}{\mu}[1 - e^{-\mu t}] \tag{9}$$

in which $C =$ a proportionality constant. Eqn. 9 is identical to Eqn. 3 with $L_b = CN_0/\mu$ and $K_b = \mu$, and represents the classic first stage BOD.

Similarly, if the change in bacterial population is assumed to follow a simple birth process, Eqn. 5 would be obtained. Consider now a nonhomogeneous birth and death process in which the birth rate is constant but the death rate increases linearly with time. The mean bacterial population is then

$$N = N_0 e^{\lambda t - \mu t^2/2} \tag{10}$$

in which $\lambda =$ constant birth rate; and $\mu t =$ death rate increasing linearly with time (Bailey 1964). Again, assuming that the oxygen demand is proportional to the total bacterial life,

$$\frac{dy}{dt} = CN_0 e^{\lambda t - \mu t^2/2} \tag{11}$$

or integrating

$$y = \alpha\left[\operatorname{erf}\left(\frac{\lambda}{\sqrt{2\mu}}\right) + \operatorname{erf}\left(\sqrt{\frac{\mu}{2}}\,t - \frac{\lambda}{\sqrt{2\mu}}\right)\right] \tag{12}$$

in which

$$\alpha = CN_0\sqrt{\pi/\mu}\, e^{\lambda^2/2\mu}$$

The error function is defined by

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{-u^2}\,du \tag{13}$$

in which $z =$ argument of the error function; and $u =$ dummy variable of integration.

Note that it is possible to describe the entire growth curve shown in Fig. 1 by Eqn. 12, which has three parameters α, λ and μ that must be determined by nonlinear regression methods. The model represented by Eqn. 12 will be referred to as the three-parameter second stage BOD.

ESTIMATION OF MODEL PARAMETERS

1. FIVE-PARAMETER BOD MODEL

Two independent least squares schemes will be considered for the regions $t < t_0$ and $t \geqslant t_0$. For $t < t_0$, the function which has to be minimized is

$$S = \sum_{i=1}^{m}\{y_i - L_a[e^{K_a t_i} - 1]\}^2 \tag{14}$$

in which $S =$ the sum of the squares of the difference between observed and computed values of the nitrogenous BOD, i.e. error sum of squares; $y_i =$ observed BOD; $t_i =$ time of the ith observation; $i =$ the summation index; and $m =$ number of observations for which $t_i < t_0$. To determine the values of L_a and K_a for which S becomes a minimum, the equations $\partial S/\partial L_a = 0$ and $\partial S/\partial K_a = 0$ must be solved simultaneously. Since Eqn. 14 is nonlinear in K_a, explicit solutions are not possible, and an iterative scheme must be sought. Although several nonlinear least squares methods are available for this purpose, a procedure similar to the one developed by Reed & Theriault (1931) for the determination of the deoxygenation constant in the exertion of carbonaceous BOD will be followed.

The values of K_a at the end of two successive iterations are considered to differ by δK_a, i.e.

$$K_{a(j+1)} = K_{a_j} + \delta K_{a_j} \tag{15}$$

in which j = the iteration number. Substitution of Eqn. 15 into Eqn. 14 gives the value of S for the jth iteration as

$$S = \sum_{i=1}^{m} \{y_i - L_a[e^{K_{aj}t_i} e^{\delta K_{aj}t_i} - 1]\}^2 \tag{16}$$

Assuming that the product $\delta K_{aj} t_i$ is small, the term $\exp(\delta K_{aj} t_i)$ can be approximated by the first two terms of the Taylor series expansion, and Eqn. 16 can be written as

$$S = \sum_{i=1}^{m} \{y_i - c_1 f_{1_i} - c_2 f_{2_i}\}^2 \tag{17}$$

in which

$$f_{1_i} = e^{K_{aj}t_i} - 1 \tag{18a}$$

$$f_{2_i} = t_i e^{K_{aj}t_i} \tag{18b}$$

$$c_1 = L_a \tag{18c}$$

$$c_2 = \delta K_{a_j} L_a \tag{18d}$$

Error sum of squares given by Eqn. 17 is now linear in c_1 and c_2, and from the conditions $\delta S/\delta c_1 = 0$ and $\delta S/\delta c_2 = 0$, c_1 and c_2 can be determined as

$$c_1 = \frac{1}{D_1}[(\Sigma y f_1)(\Sigma f_2^2) - (\Sigma f_1 f_2)(\Sigma y f_2)] \tag{19a}$$

$$c_2 = \frac{1}{D_1}[(\Sigma f_1^2)(\Sigma y f_2) - (\Sigma y f_1)(\Sigma f_1 f_2)] \tag{19b}$$

in which

$$D_1 = (\Sigma f_1^2)(\Sigma f_2^2) - (\Sigma f_1 f_2)^2 \tag{20}$$

As usual, summations run from $i = 1$ to m. Once c_1 and c_2 are determined, the value of K_a can be corrected at each iteration by $\delta K_{aj} = c_2/c_1$, and the new value of K_a for the next iteration can be calculated by Eqn. 15. The procedure is repeated until δK_a becomes smaller than a predetermined value.

It is emphasized that the least squares scheme described not only requires an initial estimate of K_a, it also requires an estimate of t_0 for the determination of m.

Now, in considering the data for which $t \geqslant t_0$, the error sum of squares can be written as

$$S = \sum_{i=m+1}^{n} \{y_i - L_a[e^{K_a t_0} - 1] - L_b[1 - e^{-K_b(t_i - t_0)}]\}^2 \tag{21}$$

in which n = total number of observations. At this time, the parameters L_a and K_a in Eqn. 16 will be considered as known. Following a similar procedure as before, the error sum of squares is

$$S = \sum_{i=m+1}^{n} \{y_i - c_3 - c_4 f_{3_i} - c_5 f_{4_i}\}^2 \tag{22}$$

in which

$$f_{3_i} = e^{-K_{bj}(t_i - t_0)} \tag{23a}$$

$$f_{4_i} = (t_i - t_0)\, e^{-K_{bj}(t_i - t_0)} \tag{23b}$$

$$c_3 = L_a(e^{K_a t_0} - 1) + L_b \tag{23c}$$

$$c_4 = -L_b \tag{23d}$$

$$c_5 = L_b \delta K_{b_j} \tag{23e}$$

and

$$K_b(j+1) = K_{b_j} + \delta K_{b_j} \tag{24}$$

Eqn. 22 is linear in c_3, c_4 and c_5, and setting $\partial S/\partial c_3 = 0$, $\partial S/\partial c_4 = 0$, $\partial S/\partial c_5 = 0$, the least squares parameters c_3, c_4 and c_5 will take the following values in determinant form:

$$c_3 = \frac{1}{D_2} \begin{vmatrix} \Sigma y & \Sigma f_3 & \Sigma f_4 \\ \Sigma y f_3 & \Sigma f_3^2 & \Sigma f_3 f_4 \\ \Sigma y f_4 & \Sigma y f_4 & \Sigma f_4^2 \end{vmatrix} \tag{25a}$$

$$c_4 = \frac{1}{D_2} \begin{vmatrix} (n-m) & \Sigma y & \Sigma f_4 \\ \Sigma f_3 & \Sigma y f_3 & \Sigma f_3 f_4 \\ \Sigma f_4 & \Sigma y f_4 & \Sigma f_4^2 \end{vmatrix} \tag{25b}$$

$$c_5 = \frac{1}{D_2} \begin{vmatrix} (n-m) & \Sigma f_3 & \Sigma y \\ \Sigma f_3 & \Sigma f_3^2 & \Sigma y f_3 \\ \Sigma f_4 & \Sigma f_3 f_4 & \Sigma y f_4 \end{vmatrix} \tag{25c}$$

in which

$$D_2 = \begin{vmatrix} (n-m) & \Sigma f_3 & \Sigma f_4 \\ \Sigma f_3 & \Sigma f_3^2 & \Sigma f_3 f_4 \\ \Sigma f_4 & \Sigma f_3 f_4 & \Sigma f_4^2 \end{vmatrix} \tag{26}$$

In the above equations, summations run from $i = m + 1$ to n. The value of δK_{bj} at the end of each iteration can be determined as $\delta K_{bj} = -c_5/c_4$, and the procedure is repeated until δK_{bj} is sufficiently small.

Upon completion of this set of iterations, a new estimate for t_0 can be made from Eqn. 23c as

$$t_0 = \frac{1}{K_a} \ln\left(1 + \frac{c_3 - L_b}{L_a}\right) \tag{27}$$

With this new value of t_0, the procedure must be repeated for both regions $t < t_0$ and $t \geqslant t_0$ and the least squares parameters c_1, c_2, c_3, c_4 and c_5 must be determined. When the difference between two successive estimates of t_0 is sufficiently small, the current values of the parameters K_a, K_b and t_0 are identified as the final estimates. The corresponding estimates for L_a and L_b are $L_a = c_1$ and $L_b = -c_4$.

2. THREE-PARAMETER BOD MODEL

Recall that Eqn. 12 represents the mathematical model describing the nitrogenous BOD exertion. If BOD exertion y is plotted against time t, a point of inflection will occur at a critical time which we will again refer to as t_0. Differentiating Eqn. 11 and setting it equal to zero at $t = t_0$ yield the relationship between birth and death rate parameters as

$$\frac{\lambda}{\mu} = t_0 \tag{28}$$

Combining Eqns. 28 and 12, the BOD exertion can be written as

$$y = \alpha[\mathrm{erf}(\sqrt{\mu/2}\, t_0) + \mathrm{erf}(\sqrt{\mu/2}\, t - \sqrt{\mu/2}\, t_0)] \tag{29}$$

The error sum of squares is then

$$S = \sum_{i=1}^{n} \{y_i - \alpha\, \mathrm{erf}(\sqrt{\mu/2}\, t_0) - \alpha\, \mathrm{erf}(\sqrt{\mu/2}\, t_i - \sqrt{\mu/2}\, t_0)\}^2 \tag{30}$$

To determine the values of α and μ for which S becomes a minimum, the equations $\partial S/\partial\alpha = 0$ and $\partial s/\partial\mu = 0$ are both solved for α and the so-called normal equations are obtained (Barnwell 1980).

$$\alpha = \frac{S_1}{S_2} \tag{31}$$

$$\alpha = \frac{S_3}{S_4} \tag{32}$$

in which

$$S_1 = \Sigma y[\mathrm{erf}(\sqrt{\mu/2}\, t_0 + \mathrm{erf}(\sqrt{\mu/2}\, t - \sqrt{\mu/2}\, t_0)] \tag{33a}$$

$$S_2 = \Sigma[\mathrm{erf}(\sqrt{\mu/2}\, t_0) + \mathrm{erf}(\sqrt{\mu/2}\, t - \sqrt{\mu/2}\, t_0)]^2 \tag{33b}$$

$$S_3 = \Sigma y[t_0\, e^{-\mu t_0^2/2} + (t - t_0)\, e^{-(\sqrt{\mu/2}\, t - \sqrt{\mu/2}\, t_0)^2}] \tag{33c}$$

$$S_4 = \Sigma[\mathrm{erf}(\sqrt{\mu/2}\, t_0) + \mathrm{erf}(\sqrt{\mu/2}\, t - \sqrt{\mu/2}\, t_0)] \times [t_0\, e^{-\mu t_0^2/2} + (t - t_0)\, e^{-(\sqrt{\mu/2}\, t - \sqrt{\mu/2}\, t_0)^2}] \tag{33d}$$

In all these equations summations run from $i = 1$ to n, the total number of observations.

In the computation of the error functions in Eqn. 33 the following rational approximation given by Abramowitz & Stegun (1970) can be used:

$$\mathrm{erf}(z) = 1 - e^{-z^2} \sum_{i=1}^{5} a_i(1 + 0.32759z)^{-i} + \epsilon(z), \quad z > 0 \tag{34}$$

in which $a_1 = 0.25483$, $a_2 = -0.28450$, $a_3 = 1.42141$, $a_4 = -1.45315$, and $a_5 = 1.06141$ with $|\epsilon(z)| \leqslant 1.5 \times 10^{-7}$.

It should be noted that $\text{erf}(-x) = -\text{erf}(x)$. In this respect, when Eqn. 34 is used for the computation of error functions in Eqn. 33, the terms $\text{erf}(\sqrt{\mu/2}\,t - \sqrt{\mu/2}\,t_0$ must be replaced by $\text{erf}(\sqrt{\mu/2}\,t_0 - \sqrt{\mu/2}\,t)$ for $t < t_0$.

The value of μ, denoted $\hat{\mu}$, that gives the same value of α in both Eqns. 31 and 32 is the least squares estimate of μ. To determine $\hat{\mu}$, the function $g(\mu)$ is defined as the difference between the values of α as obtained from Eqns. 31 and 32, i.e.,

$$g(\mu) = S_1/S_2 - S_3/S_4 \tag{35}$$

The value of μ that makes $g(\mu) = 0$ is the least squares estimate $\hat{\mu}$. Eqn. 35 can be solved by iterative procedures, e.g. by the Newton's method, which requires an initial estimate for μ be made. These iterative schemes also require the derivative of the function $g(\mu)$ which can be conveniently computed as $g'(\mu) = [g(\mu + \Delta\mu) - g(\mu)]/\Delta\mu$ in which $\Delta\mu$ is a sufficiently small increment.

The procedure described requires a knowledge of t_0. With the estimated value of μ, the birth rate λ can be determined by Eqn. 28. If the parameters of the five-parameter model are known, the initial estimate of t_0 can be taken equal to that in the five-parameter model. Alternatively, t_0 can be directly read from a plot of y against t. Fine-tuning of the three-parameter model can be made by trial and error by assuming different values for t_0 until the absolute minimum error sum of squares defined by Eqn. 30 is obtained. The procedure of increasing t_0 by increments until an increase in S is observed, and then halfing the increment in t_0, and continuing backwards in a similar fashion until the minimum value of S is reached has been observed to give fairly short computation times. In the case studies investigated, estimation of t_0 within ± 0.1 day was sufficiently accurate.

Confidence regions and correlation coefficients

The confidence regions for the parameters of the five parameter model are expected to be similar to the confidence regions observed in the parameters of the models for carbonaceous BOD exertion. This is simply because of the close similarity between the first stage and second stage BOD models in the time intervals $t < t_0$ and $t \geqslant t_0$. The confidence regions for the three-parameter model must be investigated further.

The confidence contours are defined by considering the error sum of squares as constant. For the nonlinear least squares, an approximate $100(1-q)\%$ confidence contour is given by Bates & Watts (1988) as

$$Sq = S(\hat{\alpha}, \hat{\mu})\left\{1 + \frac{p}{n-p} F(p, n-p, 1-q)\right\} \tag{36}$$

in which $p =$ the number of model parameters; $n =$ the number of observations; $q =$ the confidence level; $F =$ the inverse function of an F distribution; and $S(\hat{\alpha}, \hat{\mu}) =$ minimum sum of squares.

Considering t_0 as known and setting $p = 2$ for the three-parameter BOD model, the inverse of an F distribution is given by

$$F(2, n-1, 1-q) = \frac{n-2}{2}[q^{-2/(n-2)} - 1] \tag{37}$$

The substitution of Eqn. 37 into Eqn. 36 gives the approximate $100(1-q)\%$

confidence contours as

$$Sq = S(\hat{\alpha}, \hat{\mu})[q^{-2/(n-2)}] \tag{38}$$

to simplify the notation, if we let

$$X_i = \text{erf}\,[\sqrt{\mu/2}\,t_0 + \text{erf}\,(\sqrt{\mu/2}\,t_i - \sqrt{\mu/2}\,t_0)] \tag{39}$$

then the values of α and μ defining the confidence contours can be determined from

$$Sq = \sum_{i=1}^{n} \{y_i - \alpha X_i\}^2 \tag{40}$$

Thus, for μ given the two solutions of α have the form

$$\alpha = \frac{\Sigma Xy \pm [(\Sigma Xy)^2 - (\Sigma X)(\Sigma y - Sq)]^{1/2}}{\Sigma X^2} \tag{41}$$

The value of *Sq* in Eqn. 41 must be computed from Eqn. 38. It is noted again that t_0 was assumed to be known a priori. If the variations in t_0 are to be considered, the number of model parameters is taken as $p = 3$ in Eqn. 36, and a confidence contour for different values of t_0 can then be determined.

The nonlinear correlation coefficient for both models can simply be computed as

$$r = \pm\sqrt{\frac{\Sigma(\hat{y} - \bar{y})^2}{\Sigma(y - \bar{y})^2}} \tag{42}$$

in which r = correlation coefficient; $\hat{y}$ = estimated value of BOD; and $\bar{y}$ = mean value of BOD for the whole series of data obtained from the test (Bates & Watts 1988).

APPLICATIONS

The five-parameter and three-parameter second stage BOD models were determined by the least squares schemes for two sets of nitrogenous BOD data reported by Courchaine (1962), two sets reported by Young (1973) and two sets of data obtained in Kuwait in 1989. The first BOD data were for 24-hour composite sample of Lansing Sewage Treatment Plant effluent which is an activated sludge effluent. The second data were obtained from samples collected from Grand River, Michigan at a point one mile downstream of the City Sewage Treatment Plant. Both of Young's data were for the same trickling filter effluent. The Kuwait data were obtained from the day-time grab samples of raw sewage which had undergone partial anaerobic breakdown, and facultative waste stabilization pond effluent, respectively. All BOD samples were incubated at 20°C and two sets of measurements were made simultaneously, one for the measurement of total BOD, i.e. carbonaceous plus the nitrogenous BOD, and the other for the measurement of carbonaceous BOD in which nitrification was inhibited. The difference in the two sets of measurements gave the nitrogenous BOD. Courchaine (1962) used methylene blue as the nitrification inhibitor, Young (1973) used allylthiourea (ATU) for sample 1 and a product labelled N-Hib for sample 2. In the tests performed in Kuwait 2-chloro-6-(trichloro methyl) pyridine (TCMP) was used for this purpose (Standard methods for the examination of water and wastewater 1980).

Table 1 lists the influent ammonia-nitrogen and nitrite nitrogen concentrations,

Table 1. Influent nitrogen concentration and parameters of five-parameter and three-parameter nitrogenous BOD models.

	Lansing sewage treatment plant effluent	Grand River, Michigan	trickling filter effluent sample 1	trickling filter effluent sample 2	raw sewage Kuwait	facultative pond effluent Kuwait
Influent nitrogen concentrations						
Ammonia nitrogen (mg/l)	15	NA*	52.8	52.8	80	14
Nitrite nitrogen (mg/l)	0	NA*	0.41	0.41	1.2	0.8
Five-parameter model						
K_a (day^{-1})	0.240	0.294	0.467	0.435	0.050	0.241
L_a (mg/l)	0.99	0.26	9.25	11.9	89.5	0.29
K_b (day^{-1})	0.513	0.202	0.312	0.454	0.437	0.094
L_b (mg/l)	69.5	9.04	28.9	49.0	131.4	34.2
t_0 (day)	13.8	9.8	6.3	6.0	18.7	18.2
S (mg^2/l^2)	5.71	0.340	286.5	460.1	524.9	22.2
r	0.998	0.998	0.980	0.972	0.987	0.984
Three-parameter model						
α (mg/l)	47.0	6.22	95.1	97.6	155.2	22.3
λ (day^{-1})	2.68	0.698	1.86	1.58	0.278	0.693
μ (day^{-2})	0.185	0.0629	0.372	0.322	0.0159	0.0375
t_0 (day)	14.5	11.1	5.0	4.9	17.5	18.5
S (mg^2/l^2)	135.1	0.368	126.8	222.0	3692.0	17.9
r	0.997	0.997	0.998	0.982	0.985	0.986
95% conf. intervals for α	41.5–52.0	6.05–6.43	93.6–96.7	95.7–99.8	142.7–172.8	21.4–23.3
95% conf. intervals for λ	0.89–9.92	0.54–0.90	1.49–2.33	1.18–2.12	0.16–0.45	0.51–0.85

* Not available.

least squares estimates of the parameters of the two models, error sum of squares and correlation coefficients for each model, and the 95% confidence intervals for the parameters of the three-parameter model. The absolute minimum error sum of squares for the three-parameter model and the corresponding 95% confidence intervals were determined with the value of t_0 reported. The measured and computed nitrogenous BOD values are shown in Figs. 2 to 7 for the six cases investigated.

DISCUSSION AND CONCLUSIONS

Comparison of the values of nitrogenous BOD given in Figs. 2–7 shows that there is reasonable agreement between the measured and computed values of BOD. As evidenced by the error sum of squares listed in Table 1, the five-parameter model has performed only slightly better than the three-parameter model. The 95% confidence intervals indicate that the parameters α and λ of the three-parameter model appear to be rather correlated and imprecise. However, this should be as expected in biological processes such as nitrogenous BOD exertion, especially when the nitrogenous BOD is calculated as the difference between the total BOD and the carbonaceous BOD. The parameters of the first order decay model for the carbonaceous BOD are also known to show such an extent of correlation (Barnwell 1980). Also, the relatively wide confidence intervals for λ are rather misleading, since in the actual BOD and dissolved oxygen computations, the term $\sqrt{\lambda/2t_0}$ which has a much smaller confidence interval is used.

In the parameter estimation for the five-parameter model, the least squares scheme developed requires initial estimates of K_a, K_b and t_0. It is usual with nonlinear regression procedures of this type that the iterative scheme diverges when the initial values of K_a and K_b are chosen outside a certain range. For this model, however, the

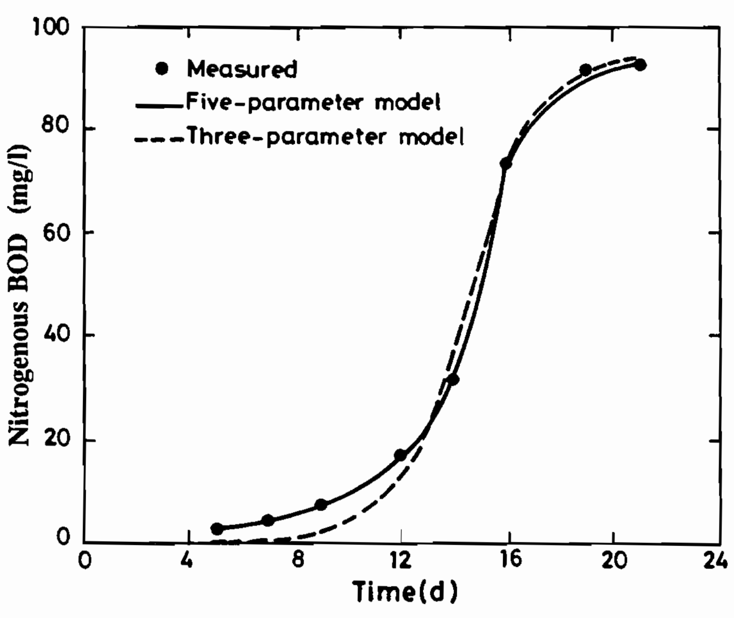

Fig. 2. Measured and computed values of nitrogenous BOD for Lansing sewage treatment plant effluent.

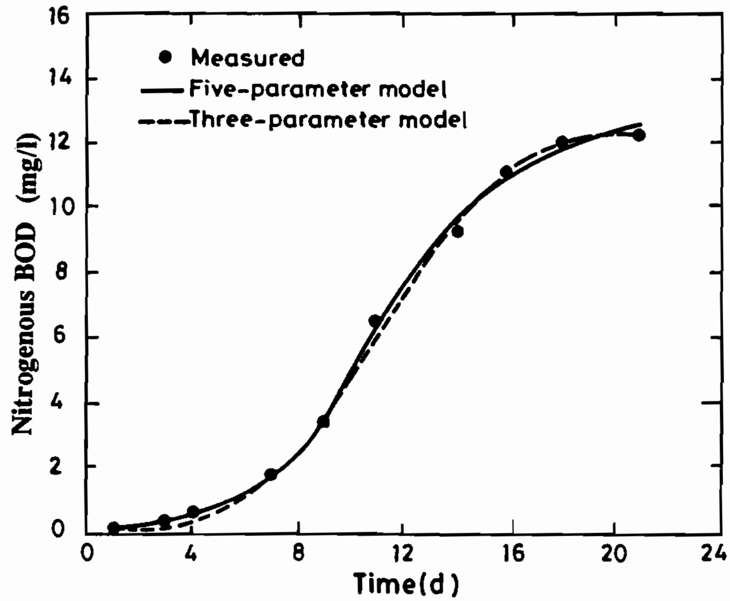

Fig. 3. Measured and computed values of nitrogenous BOD for Grand River, Michigan.

choice of the initial estimate for t_0 turns out to be more critical, and unless t_0 is chosen within the correct interval of measured t values, the least square scheme tends to diverge. In the present case, this difficulty is overcome by searching different time intervals any time divergence is observed. Typically, the mid-point of two successive t values are chosen as t_0. Obviously, too many data points increase computation time

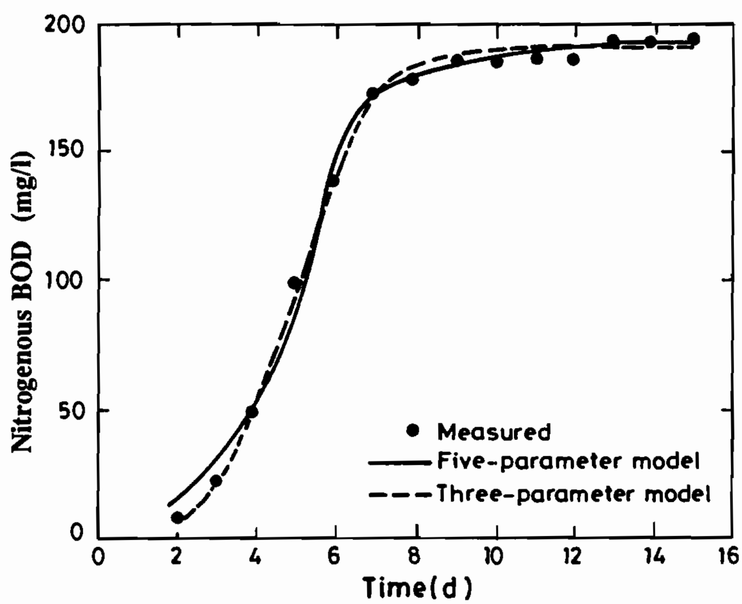

Fig. 4. Measured and computed values of nitrogenous BOD for trickling filter effluent—sample 1.

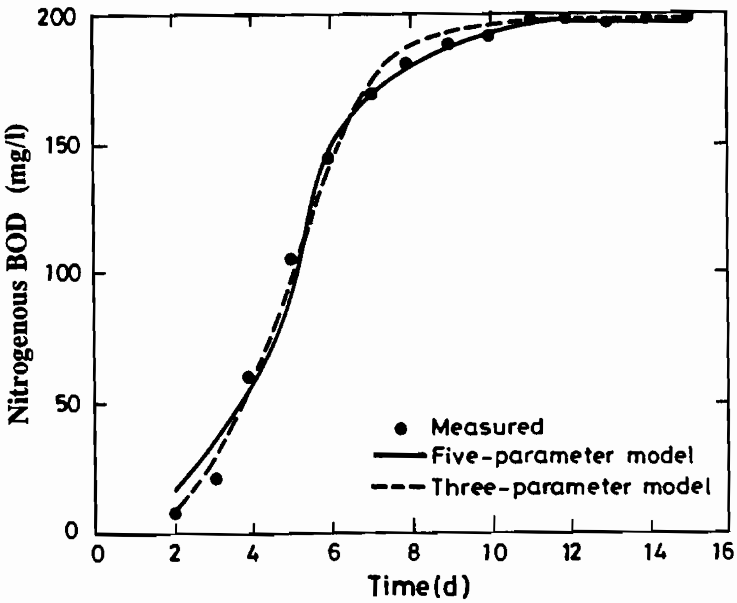

Fig. 5. Measured and computed values of nitrogenous BOD for trickling filter effluent—sample 2.

due to this searching procedure. Such difficulties are not encountered in the three-parameter BOD model. Nevertheless, for the case studies investigated, the largest computation time required was about four minutes for the five parameter model, and about two minutes for the three-parameter model. An IBM compatible 286 computer operating at 12.5 MHz was used throughout the study.

The smallest value of $\lambda/\sqrt{2\mu}$ observed in the six case studies was 1.56. For this value of $\lambda/\sqrt{2\mu}$, Eqn. (12) gives $y(t) \doteqdot 1.97\alpha$ as $t \to \infty$. For this reason, the term 2α can be conveniently referred to as the ultimate second stage BOD. For the five-parameter BOD model, ultimate second stage BOD can be expressed as $L_a[e^{Kato} - 1] + L_b$. It should be noted that the ultimate BOD is limited by the amount of oxidizable nitrogen available. Nitrification is a two-stage reaction in which first ammonia is oxidized to nitrite and then nitrite is oxidized to nitrate while some of the reduced nitrogen is assimilated as cell material. It is now well established that 1 mg/l of ammonia nitrogen requires a total of about 4.33 mg/l of oxygen. Any additional nitrite present in the water requires about 1.11 mg/l of oxygen per 1 mg/l of nitrite nitrogen (Young 1973). Inspection of the values given in Table 1 indicates that with the exception of the Lansing Sewage Treatment Plant effluent, the ultimate second stage BOD is less than the total oxygen required for the oxidation of ammonia and nitrite nitrogen. The reason for the discrepancy in the Lansing Sewage Treatment Plant effluent is possible due to the use of methylene blue as the nitrification inhibitor. It is known that methylene blue interferes with the dissolved oxygen and nitrite determinations and affects the carbonaceous oxygen demand (Young 1973).

Inspection of Figs. 2–7 shows that a significant amount of nitrogenous BOD is exerted until the critical time t_0. For the six cases studied, the percentage of BOD exerted until t_0 to ultimate second stage BOD varied between 27 and 85%. In this

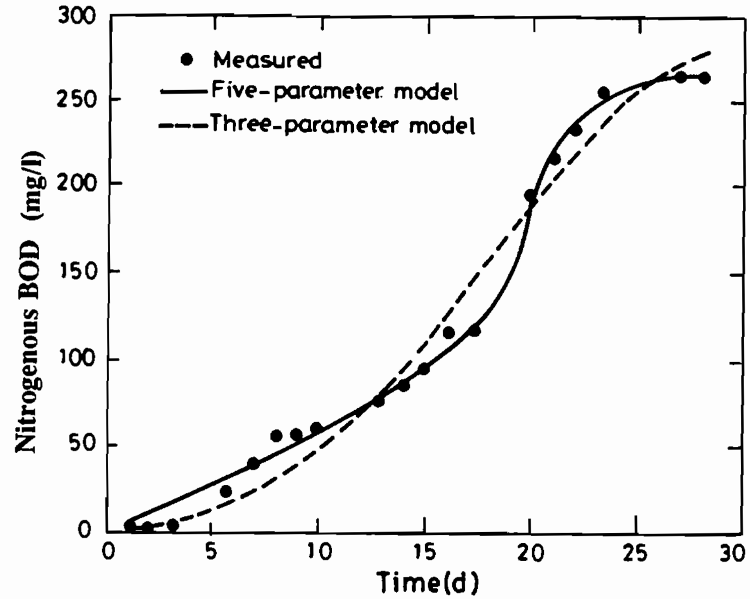

Fig. 6. Measured and computed values of nitrogenous BOD for Kuwait raw sewage.

respect, ignoring oxygen consumed until t_0 and using models such as those given by Eqn. 4 are not justified.

It can be concluded that both models developed can predict nitrogenous oxygen demand with reasonable accuracy. The five-parameter model performs slightly better, but the three-parameter model is easier to implement in water quality modeling. The

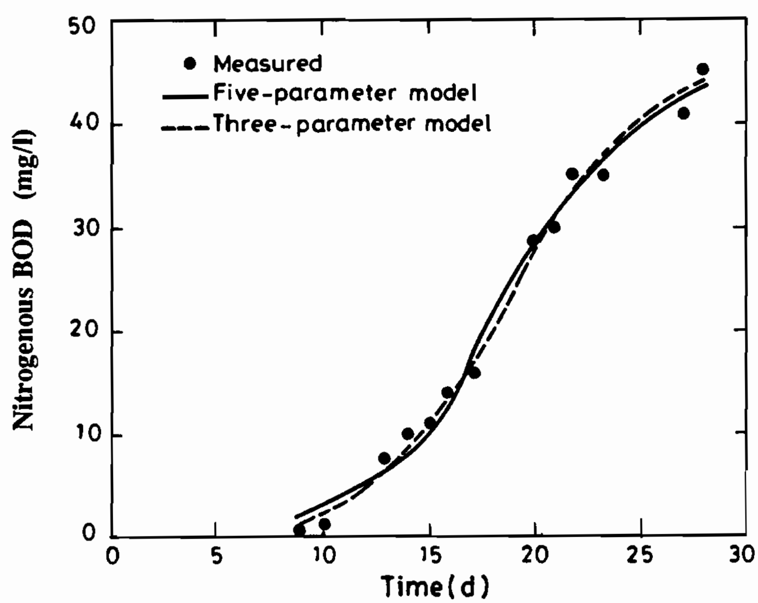

Fig. 7. Measured and computed values of nitrogenous BOD for Kuwait facultative pond effluent.

parameters of both models can be estimated by nonlinear least squares schemes. Effect of environmental factors such as temperature, pH and inhibitory materials on model parameters was not investigated here.

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التمثيل الرياضي لعمليات تحويل النيتروجين في الإختبـارات على الـطلب البيوكيميـائي للأكسجين

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خلاصة

يظهر الطلب على الأكسجين عند إمتصاص مركبات النيتروجين الموجودة في المياه بواسطة البكتيريا التي تنتفع بالمواد الغير عضوية.

إن الطلب على الأكسجين في العمليات البيوكيميائية المتعلقة بالمواد النيتروجينية أبطأ من المواد الكربونية ولذا فأنها تستغرق عدة أيام قبل إتمامها.

إن عملية تحويل المركبات النيتروجينية مهمة وعلى وجه الخصوص في ما يتعلق بالنفايات الملقاة في المياه والتي تم تبذيرها بالبكتيريا النيتروجينية كما أنها تتأثر كثيرا بمعدل النمو لهذه الأحياء.

وقد تم تطوير نموذجين رياضيين قائمين على النمو الميكروبي وذلك لتمثيل الطلب النيتروجيني على الأكسجين: النموذج الأول هو تعديل لنموذج مونود وفيه تم معالجة كـل من حالـة النمو والإضمحلال على حدة. أما النموذج الآخر فهو نموذج غير متجانس للولادة والوفاة حيث أن معدل الولادة ثابت ومعدل الوفاة يتزايد خطيا مع الزمن.

وتم إيجاد المعاملات في النماذج الغير خطية بطريقة حساب أدنى التربيعات وإعتمادا على ستة مجموعات من القراءات للطلب النيتروجيني للأكسجين في العمليات البيوكيميائية. وتمثـل هذه القراءات في الخارج الحمأة المنشطة ومياه المجاري المعالجة والمختلطة بمياه النهر وعينـات المياه الخارجة بعد مرشحين ذو إنسياب خطي رفيع وعينات مياه المجاري الغير معالجة بالإضافة الى المياه الخارجة من بحيرات مختارة.

وقد وجد بأن النموذجين يمثلان الطلب النيتروجيني على الأكسجين في العمليات البيوكيميائية بشكل جيد.