Short communication

On the determination of the kinetic parameters for the BOD test

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Abstract

One of the most common tests for the determination of the organic content of wastewater is the biochemical oxygen demand (BOD). The kinetic parameters k (rate constant) and L (ultimate demand) can be estimated by different methods, such as: non-linear fitting, linear fitting of modified expressions of the BOD equation, and the Thomas method among others. In this note, three of the most common methods for the determination of k and L are compared. Particular attention is paid to the accuracy of each method.

Introduction

The organic content of wastewater can be determined by various methods. The most commonly used are methods that measure the oxygen consumption, although the determination of organic carbon is also used. In the first method the amount of oxygen required to degrade the organic content of an effluent is estimated either using the procedure of biochemical oxygen demand (BOD) or chemical oxygen demand (COD). The COD is based on a fairly fast chemical oxidation, but is not representative of the biological degradation that occurs in the environment.

The BOD of a wastewater is estimated by measuring the oxygen consumed during the degradation of organic matter by the amount of dissolved microbial flora present in the water or the effluent stream. The most common procedure is the dilution method, which basically consists of diluting the water (depending on the degree of contamination) with a nutrient solution saturated with air. Then the solutions are stored in the dark in closed bottles and the dissolved oxygen is measured periodically. Usually, 5 d are used for the test, and the results are reported as BOD_5.

Periodical measurements of the dissolved oxygen (not only at the start and end of the 5 d) are required to ensure that the procedure is being carried out correctly and to detect possible errors such as an excessive dilution, presence of toxic compounds or the lack of a microbial population sufficiently adapted.

Although other modelling approaches have been presented (Adrian and Sanders, 1992; Mayou, 1990), the BOD curve can be described by a first-order kinetics equation (Metcalff and Eddy, 1977):

$$\frac{dL}{dt} = -kL \tag{1}$$

Eq. (1) is easily integrated to yield :

$$y = L_0 \, (1 - \exp(-kt)) \tag{2}$$

or:

$$y = L_0 \, (1 - 10^{-k_{10} \, t}) \tag{3}$$

where:

- y = amount of oxygen consumed (or BOD) at time t
- t = time elapsed since the start of the assay
- L_0 = total amount of oxygen consumed in the reaction (or ultimate BOD)
- k , k_{10} = reaction constants.

For the determination of k (or k_{10}) and L_0 three methods are commonly used: the linear regression method, the Thomas method, and the non-linear regression method.

In the linear (Metcalff and Eddy, 1977) and the non-linear (Marquardt, 1963) regression methods the coefficients are estimated by minimising the square of the sum of the errors between the experimental values and the ones predicted by each method.

The method of Thomas (Thomas, 1950) is based on functions similarity. In this method, $(t/y)^{1/3}$ is plotted as ordinate vs. t as abscissa, and fitting the points to a straight line with intercept a and slope b. This results in a straight line. The parameters are then estimated using the slope (b) and the intercept (a) of this line:

$$k_{10} = 2.61 \, \frac{b}{a} \tag{4}$$

$$L_0 = \frac{1}{2.3 \; k_{10} \; a^3} \tag{5}$$

More details on each method can be found in the references. The goal of this work is to compare each method of parameter estimation, with particular attention to the goodness of fit.

Materials and methods

The BOD analyses were made on food-processing effluents (bakeries and fish-processing plants) with BOD_5 ranging from 629 mg·ℓ$^{-1}$ to 938 mg·ℓ$^{-1}$. The samples were collected and the BOD test carried out according to *Standard Methods* (1980). The oxygen content was measured using the azide method (Winkler modification).

The calculations were carried out in an electronic spreadsheet for the linear regression and Thomas methods, and by means of an optimisation program for the non-linear regression.

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TABLE 1
NUMERICAL VALUES OF PARAMETERS OBTAINED BY THE THREE DIFFERENT ESTIMATION PROCEDURES

	Parameter	Least sq.	Thomas	Non-linear
curve 1	k	0.417	0.3299	0.40161
curve 2	k	0.386	0.3450	0.38959
curve 3	k	0.376	0.3579	0.38089
curve 4	k	0.661	0.5556	0.62346
curve 5	k	0.545	0.5215	0.55783
curve 6	k	0.514	0.4332	0.49477
curve 7	k	0.469	0.4065	0.45732
curve 1	L_o	753.611	825.50	748.04
curve 2	L_o	967.881	1 009.22	946.19
curve 3	L_o	1 023.712	1 042.98	1003.4
curve 4	L_o	849.375	902.53	845.23
curve 5	L_o	993.819	1 017.06	968.23
curve 6	L_o	1 032.315	1 092.53	1 023.0
curve 7	L_o	1 077.287	1 136.21	1 066.3

Results and discussion

The values of the kinetic coefficients for each assay determined by the three different methods are listed in Table 1. It can be seen that there are marked differences among the values of the constants calculated by different methods. However, a comparison by inspection does not allow one to draw conclusions. To assess the goodness of fit for each method the following values were calculated: the total error (sum of the squares of the errors between the values predicted by each method and the experimental values, or err^2):

$$err^2 = \sum_{i=1}^{n} (y_{obs} - y_{calc})^2 \qquad (6)$$

the coefficient of determination (CD):

$$\frac{\sum_{i=1}^{n}\left(Yobs_i - \overline{Y}obs\right)^2 - \sum_{i=1}^{n}\left(Yobs_i - Ycal_i\right)^2}{\sum_{i=1}^{n}\left(Yobs_i - \overline{Y}obs\right)^2} \qquad (7)$$

and the model selection criterion (MSC) (Akaike, 1976):

$$MSC = \ln\left(\frac{\sum_{i=1}^{n}\left(Yobs_i - \overline{Y}obs\right)^2}{\sum_{i=1}^{n}\left(Yobs_i - Ycal_i\right)^2}\right) - \frac{2p}{n} \qquad (8)$$

where:

$Yobs_i$ = observed (experimental) values
$\overline{Y}obs$ = average of observed (experimental) values
$Ycal_i$ = calculated values of each fitting procedure
p = number of parameters
n = number of data points

The total error and the CD are more common than the MSC. However, the MSC is not dependent on the numerical value of the measurements, and places a burden on models with more parameters and is therefore a more objective measurement of the goodness of fit.

The analysis of goodness of fit was made for each of the fitting methods and each curve. The results are shown in Table 2. From these results, it is clear that using a non-linear regression method results (in all cases) in the smallest error, the highest CD and the highest MSC. Figure 1 shows the experimental data for all runs together with the fitting that resulted when plotting the non-linear method data points.

The least squares method can be easily implemented in an electronic spreadsheet, and most plotting packages have it built in too. Its drawback is that it gives a larger error due to the discrete estimation of the slope which is made at each point.

The Thomas method (which is also easy to implement) originated from the similarity in shapes of an arbitrary function with that of the BOD curve, which is not always true.

Although it can be argued that a non-linear method is more difficult to implement, the extended use of computers and the existence of computer packages or routines for non-linear parameter estimation have made its implementation much simpler in recent years. Therefore, it should be the method of choice when making BOD parameters estimation.

TABLE 2
COMPARISON OF GOODNESS OF FIT FOR EACH EXPERIMENT AND EACH ESTIMATION PROCEDURE

Curve	Least sq.	Thomas	Non-linear
SS: Sum of the squares of the errors			
1	2 808.8	2 962.5	2 005.2
2	2 851.8	2 792.2	2 160.1
3	958.4	850.3	513.5
4	1 714.9	3 069.5	337.2
5	2 260.2	3 472.5	1 293.6
6	3 864.9	3 818.3	2 171.0
7	14 459.0	16 965.3	8 480.6
CD: coefficient of determination			
1	0.99096	0.99047	0.99355
2	0.99407	0.99419	0.99551
3	0.99817	0.99838	0.99902
4	0.99642	0.99359	0.99930
5	0.99621	0.99415	0.99783
6	0.99402	0.99409	0.99664
7	0.99578	0.99556	0.99770
MSC: model selection criterion			
1	4.04	3.39	4.38
2	4.46	4.48	4.74
3	5.64	5.76	6.26
4	4.96	4.38	6.59
5	4.91	4.48	5.47
6	4.45	4.46	5.03
7	4.80	4.75	5.41

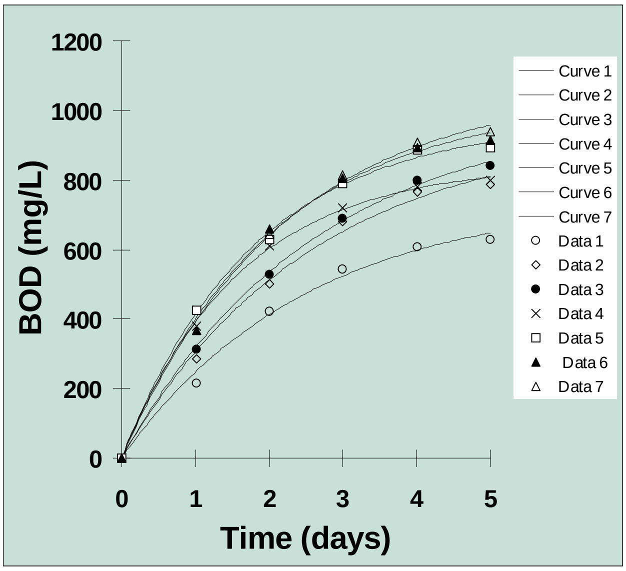

Figure 1
Predicted (continuous lines) and experimental (data points) values for the curves of each experiment. The predicted values correspond to the non-linear fitting of the data.

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