On the determination of the kinetic parameters for the BOD test

Guillermo Cutrera, Liliana Manfredi, Carlos E del Valle and J Froilán González*
Facultad de Ingenieria, Univ. Nac. Mar del Plata, Juan B. Justo 4302, 7600 Mar del Plata - Argentina

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 :

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

or:

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

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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* To whom all correspondence should be addressed.
☎(+54)(23) 81-6600; fax (+54)(23) 81-0046; e-mail froilan@fi.mdp.edu.ar