DETERMINATION OF CONSTANTS OF BOD MODELS

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Abstract - The biochemical oxygen demand (BOD) is the amount of oxygen in mg/L required to stabilize polluted water completely by means of an aerobic process. The reactions occur in the BOD bottle in laboratory as well as in streams in field and are very complex. The BOD models can be the first order, the second order, the half order, or a mixture of these. This paper pertains to the evaluation of the First order and Second order BOD models. In addition, the process of computation of the BOD rate constant k and ultimate BOD L0 using the first order as well as the second order BOD models is also presented in this paper. A solution to the second order equation is presented. Both equations are applied to experimental data and the results are compared.

Keywords - Biochemical oxygen demand, First order, Second order, BOD models.

I. INTRODUCTION

Biochemical oxygen demand is the amount of oxygen required for the micro-organisms to carry out biological decomposition of dissolved solids or organic matter in the wastewater under aerobic conditions and at standard temperature. The BOD is usually proportional to the amount of organic matter present in a wastewater and, therefore, is a measure of the strength of the waste.

Biodegradable organic matter is one of the important pollution parameter for water and wastewater. Being heterogeneous (suspended, colloidal and dissolved forms) and being composed of a wide variety of compounds, it is very difficult to have a single direct method for estimating its organic matter concentration in any water or wastewater sample. Because of this reason, indirect methods like biochemical oxygen demand (BOD), chemical oxygen demand (COD) etc. are adopted for the measurement of organic matter concentration. These methods measure the organic matter concentration through estimating the amount of oxygen required for its complete oxidation.

The determination of the BOD rate constant is important for understanding the nature of the wastewater. In case of discharging this wastewater into streams, the rate constant would help in predicting the impacts of discharging the wastewater: on the aquatic life in the stream, on the dissolved oxygen values in the stream, and on the BOD values in the stream. BOD data have historically been important in both wastewater treatment process and natural water quality applications, and continue to be utilized. However, given the limited time frames over which data sets are typically available, and the fact that tests are rarely run to completion, mathematical techniques for the prediction of maximum cumulative oxygen uptake are required, and good estimates of k values is necessary for model implementation. The development of the first order chemical reaction equation for the BOD curve is presented. The methods for solution of this equation are outlined. A solution of second order chemical reaction is presented. The experimental data is used to analysis the results. The comparison of results is done with the first order equation.

II. ESTIMATION OF BOD KINETIC PARAMETERS

Results of the serial BOD tests were used in the least squares method for estimating the BOD kinetics parameters (k and L0). Evaluation of the methods was done through calculating and comparing the sum of the absolute differences between the observed BOD and exerted BOD values.

A. First order BOD equation

The BOD rate constant, k and the ultimate first-stage BOD, L0, are usually determined by carrying out analysis of a time series of BOD data. The BOD curve, as a first approximation to measure the BOD exertion with time, is commonly described by the first-order or monomolecular expression (Marske et al., 1972; Metcalf and Eddy, 1991):

\[ y = L_0(1 - e^{-kt}) \]  

(1)

To determine the rate of oxidation at any time t, the differentiation of Eq. (1) with respect to t, after some algebraic manipulations, yields Eqs. (2) and (3).

\[ y' = kL_0e^{-kt} \]  

(2)

\[ y' = k(L_0 - y) \]  

(3)

Thus, the first-order BOD reaction, for practical purposes, can be represented as a straight line (Metcalf and Eddy, 1991):

\[ y' = kL_0 - ky \]  

(4)

Where,

\[ y' = \text{the slope of the first-order BOD curve to be fitted through all the data points;} \]
\[ k = \text{BOD reaction rate constant;} \]
\[ L_0 = \text{Ultimate first-stage BOD;} \]
\[ y = \text{BOD at any time} \ t; \text{and} \]
\[ t = \text{Time of data points.} \]

The equation (4) has the form of a straight line Eq. (5):
\[ Y = a + bX \]
\[ (5) \]

Where, \( Y = y' \), \( X = y \), \( a = kL_0 \), and \( b = -k \) that can be written as:
\[ k = -\frac{b}{a} \]
\[ L_0 = -\frac{a}{b} \]
\[ (6) \]
\[ (7) \]

The values of \( k \) and \( L_0 \) can be calculated from Equations (6) and (7). As the variables \( y \) and \( y' \) are related by a straight line Eq. (4), the method of least squares is the most commonly used method for the analysis of a time series of BOD data of wastewaters. This method determines the constants \( a \) and \( b \) of the straight line Eq. (5). The normal equations for the straight line Eq. (5) can be written as Equations (8) and (9):
\[ na + b\Sigma X = \Sigma Y \]
\[ \Sigma aX + b\Sigma X^2 = \Sigma XY \]
\[ (8) \]
\[ (9) \]

The slope \( y' \) can be calculated using Equation (10):
\[ y' = \frac{b\Delta y}{\Delta t} \]
\[ (10) \]

Where, \( n \) = Number of data points; and \( \Delta t \) = Time interval between 2 consecutive data.

B. Second order BOD Model

In the second order BOD equation, the rate of reaction depends on the concentration of two reacting substances. The rate constant has the physical significance of being the maximum rate of oxygen demand in the BOD reaction (Young and Clark, 1965). The second order BOD equation as applied to BOD data can be written as (11):
\[ d(L_0 - y)/dt = k(L_0 - y)^2 \]
\[ (11) \]

Integrating Equation (11) between the limits \( y = 0 \) to \( y \) at \( t = 0 \) to \( t \) and simplifying, one can write Eq. (12):
\[ \left(1/L_0\right) - \left(1/(L_0 - y')\right) = -kt \]
\[ (12) \]

After some algebraic manipulations, one can write Eq. (12) as Eq. (13):
\[ y = t/(A + Bt) \]
\[ (13) \]

Where,
\[ A = 1/(kl_0^2) \]
\[ B = 1/L_0 \]
\[ (14) \]
\[ (15) \]

Thus, the second order BOD reaction, for practical purposes, can be represented as a straight line (Young and Clark, 1965):
\[ y' = A + Bt \]
\[ (16) \]

Equation (16) has the form of a straight line Eq. (17):
\[ Y = A + BX \]
\[ (17) \]

Where, \( Y = t/y \), and \( X = t \).

Eliminating \( L_0 \) from Eqs. (14) and (15), one can obtain Eq. (18) for \( k \):
\[ k = B^2/A \]
\[ (18) \]

Equation (15) can be rewritten as Eq. (19) for \( L_0 \):
\[ L_0 = 1/B \]
\[ (19) \]

The values of \( k \) and \( L_0 \) for the second order BOD model can be calculated from Equations (18) and (19), respectively. As the variables \( t/y \) and \( t \) are related by a straight line Eq. (16), the method of least squares is the most commonly used method for the analysis of a time series of BOD data of wastewaters. This method determines the constants \( A \) and \( B \) of the straight line Eq. (17). The normal equations for the straight line Eq. (17) can be written as Equations (20) and (21):
\[ nA + B\Sigma X = \Sigma Y \]
\[ A\Sigma X + B\Sigma X^2 = \Sigma XY \]
\[ (20) \]
\[ (21) \]

III. EVALUATION OF THE BOD MODEL

The evaluation of both the models can be done using the evaluation criteria: The model selection criterion (MSC) is interpreted as the proportion of expected data variation that can be explained by the obtained data. Like, CD the higher the value of MSC, the higher the accuracy, validity and the good fitness of the method.

\[ MSC = ln\left(\frac{\Sigma (\Delta y)^2}{\Sigma (y - \bar{y})^2}\right) - \frac{p}{n} \]
\[ (22) \]

Where,
\[ y_o = \text{observed (experimental) values;} \]
\[ \bar{y} = \text{average of observed (experimental) values;} \]
\[ y_c = \text{calculated values of each fitting procedure;} \]
\[ p = \text{number of parameters; and} \]
\[ n = \text{number of data points.} \]

I. Analysis of BOD data

The BOD data used for the study were obtained from several sources to minimize bias that may occur in the results that the data originates from a single source (Marske et al., 1972; Rai, 2000). Time series of BOD data used in this paper are given in Table 1.

For the purpose of illustration, an analysis of a time series of BOD data number 1 using the least squares method for the first order model (FOM) and the second order model (SOM) is given Tables (2) and (3), respectively.

<table>
<thead>
<tr>
<th>Time, days</th>
<th>BOD in mg/L for data number</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>1</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Determination of Constants of Bod Models

A. First order BOD model
The calculations for the least square method for the first order BOD model is given in Table 2. Substituting the values from Table 2 in Equations (8) and (9), the normal equations become:

\[ 6a + b1595 = 330 \]  \hspace{1cm} (23)
\[ a1595 + b76000 = 472925 \]  \hspace{1cm} (24)

The solution of simultaneous Equations (23) and (24) gives \( a = 118.713 \), and \( b = -0.2397 \). Substituting the values of \( a \) and \( b \) in Equations (6) and (7), the values of \( k \) and \( L_0 \), are: \( k = 0.240 \) per day, and \( L_0 = 495.313 \) mg/L.

Table 2: First order BOD model
\[
\begin{array}{cccccc}
\text{Time, } t & y & y' & yy' & y^2 \\
1 & 120 & 95.00 & 11400.00 & 14400.00 \\
2 & 190 & 65.00 & 12350.00 & 36100.00 \\
3 & 250 & 57.50 & 14375.00 & 62500.00 \\
4 & 305 & 50.00 & 15250.00 & 93025.00 \\
5 & 350 & 37.50 & 13125.00 & 122500.00 \\
6 & 380 & 25.00 & 9500.00 & 144000.00 \\
7 & 400 & \text{---} & \text{---} & \text{---} \\
\text{Sums} & 1595.00 & 330.00 & 76000.00 & 472925.00 \\
\end{array}
\]

* Value not included in total and \( n = 6 \) is used

B. Second order BOD model
The calculations for the least square method for the second order BOD model is given in Table 3.

Table 3: Second order BOD model
\[
\begin{array}{cccc}
T & y & t/y & t^2/y \\
1 & 120 & 0.00833 & 1 \\
2 & 190 & 0.01052 & 3 \\
3 & 250 & 0.01126 & 9 \\
4 & 305 & 0.01311 & 16 \\
5 & 350 & 0.01428 & 25 \\
6 & 380 & 0.01578 & 36 \\
7 & 400 & 0.01750 & 49 \\
\text{Sums} & 199 & 0.09155 & 140 \\
\end{array}
\]

Substituting the values from Table 3 in Equations (20) and (21), the normal equations become:

\[ 7a + 28b = 0.0915 \]  \hspace{1cm} (25)
\[ 28a + 140b = 0.406 \]  \hspace{1cm} (26)

The solution of simultaneous Equations (25) and (26) gives \( A = 0.00732 \), and \( B = 0.00144 \). Substituting the values of \( A \) and \( B \) in Equations (18) and (19), the values of BOD constants are: \( k = 0.000283 \) per day, \( L_0 = 694.582 \) mg/L.

V. RESULTS AND DISCUSSION
The calculated values of \( k \) and \( L_0 \) using the least square method are given in Table 4.

Table 4: Results of BOD rate constants
\[
\begin{array}{cccc}
\text{Data} & \text{First order} & \text{Second order} \\
& k & L_0 & k & L_0 \\
I & 0.045 & 28.072 & 0.00445 & 19.314 \\
II & 0.405 & 210.183 & 0.00148 & 269.226 \\
III & 0.240 & 495.313 & 0.00028 & 694.581 \\
IV & 0.419 & 13.762 & 0.01694 & 19.081 \\
V & 0.499 & 19.314 & 0.01448 & 26.484 \\
VI & 0.220 & 7.368 & 0.00439 & 17.280 \\
VII & 0.445 & 39.290 & 0.00892 & 49.951 \\
VIII & 0.044 & 680.540 & 0.000037 & 2733.26 \\
X & 0.186 & 54.581 & 0.00162 & 82.595 \\
XI & 0.495 & 194.531 & 0.00181 & 250.855 \\
\end{array}
\]

It can be observed that the value of ultimate BOD for the second order model is higher than that for the first order model for all the twelve BOD data (Table 4).
The values of MSC for the first order BOD model and the second order BOD model were calculated using Eqs. (22). Results for all the ten BOD data are presented in Table 5.

<table>
<thead>
<tr>
<th>Data</th>
<th>MSC FOM</th>
<th>MSC SOM</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2.8595</td>
<td>4.2649</td>
<td>1.4054</td>
</tr>
<tr>
<td>II</td>
<td>3.1407</td>
<td>6.4499</td>
<td>3.3029</td>
</tr>
<tr>
<td>III</td>
<td>4.9540</td>
<td>7.5880</td>
<td>2.6603</td>
</tr>
<tr>
<td>IV</td>
<td>3.3247</td>
<td>5.9850</td>
<td>2.6603</td>
</tr>
<tr>
<td>V</td>
<td>4.6447</td>
<td>5.5609</td>
<td>0.9162</td>
</tr>
<tr>
<td>VI</td>
<td>1.8723</td>
<td>3.1950</td>
<td>1.3227</td>
</tr>
<tr>
<td>VII</td>
<td>2.7327</td>
<td>6.2513</td>
<td>3.5186</td>
</tr>
<tr>
<td>VIII</td>
<td>4.9917</td>
<td>6.5203</td>
<td>1.5286</td>
</tr>
<tr>
<td>IX</td>
<td>3.1431</td>
<td>5.0241</td>
<td>1.8810</td>
</tr>
<tr>
<td>X</td>
<td>4.0829</td>
<td>6.3419</td>
<td>2.2590</td>
</tr>
</tbody>
</table>

It is obvious that the value of Error for the second order model is less than that for the first order model for all BOD data which indicates that the second order model is better than the first order model. Further, the value of MSC for the second order model gives higher accuracy for all BOD data (Table 5). Also the difference in MSC is maximum for Data VII. Therefore; the graph of observed and calculated value of BOD is plotted for Data VII (Figure 4). The good fitness of the method which indicates that the second order model is better than the first order model. Thus, it is better to use the second order BOD model as compared to the first order BOD model.

**CONCLUSIONS**

1. The determination of the BOD rate constant using better model is important for understanding the nature of the wastewater while discharging the same into streams.
2. The rate constant would help in predicting the impacts of discharge of the wastewater on the aquatic life, the dissolved oxygen values, and BOD values in the stream.
3. The results for the analysis of the ten BOD data shows that the error for the second order BOD model is less as compared to the first order BOD model.
4. The value of MSC for the second order model gives higher accuracy for all ten data. From the analysis of ten BOD data, it can be concluded that the second order BOD model performs better than the first order BOD model.
5. It is better to use the second order BOD model as compared to the first order BOD model.

**REFERENCES**


