AN IMPROVED SOLUTION OF FIRST ORDER KINETICS FOR BIOCHEMICAL OXYGEN DEMAND

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(Received: 3rd Sept., 2016; Accepted: 5th Oct., 2016)

ABSTRACT

This paper evaluated selected Biochemical Oxygen Demand first order kinetics methods. Domestic-institutional wastewaters were collected twice in a month for three months from the Obafemi Awolowo University, Ile-Ife waste stabilization ponds. Biochemical Oxygen Demand concentrations at different days were determined using standard method. The Biochemical Oxygen Demand concentrations were used in the first order kinetics parameters (ultimate Biochemical Oxygen Demand and Biochemical Oxygen Demand reaction rate constant) determination using various methods. Accuracies of these methods were evaluated using relative error, Akaike Information Criterion (AIC), Analysis of Variance and model of selection criterion (MSC). The study revealed that ultimate Biochemical Oxygen Demand were in the range of 822 to 1813 mg/L and Biochemical Oxygen Demand removal rate was between -0.442 and -0.134/d. The average of the relative errors (%) ranged between 0.62 and 39.53, while MSC values ranged between -0.91 and 7.59 for the various methods. The results revealed that Microsoft Excel Solver provided an improved description of Biochemical Oxygen Demand removal patterns based on relative error, MSC and AIC. The study concluded that Microsoft Excel Solver, non-linear regression, least squares and Thomas’ methods were valuable methods at higher confidence levels based on lower values of AIC and relative errors and high values of MSC. Microsoft Excel Solver method was the best for solving first order kinetics of Biochemical Oxygen Demand.

Keywords: Wastewater, Environmental Engineering, Biochemical Oxygen Demand Kinetic Parameters, Statistical Evaluation

INTRODUCTION

Biological treatment processes are in use for the treatment of selected wastewaters (Orhon et al., 2000; Manson et al., 2006). The processes were found useful because their operating costs are significantly lower (Mahmood and Paice, 2006; Oke et al., 2009). Biochemical Oxygen Demand is one of the most widely used parameters for evaluating organic pollution level and quality of wastewaters. It is a measure of dissolved oxygen used by microorganisms in the biochemical oxidation of organic matters. Biochemical Oxygen Demand concentrations can be either Carbonaceous Biochemical Oxygen Demand (CBOD) or Nitrogenous Biochemical Oxygen Demand (NBOD), (Figure 1). They are the amounts of oxygen required by microorganisms to oxidize carbonaceous (organic carbon, carbohydrates) or nitrogenous (organic nitrogen, nitrate, nitrite, ammonia, etc.) compounds respectively at specified number of days and temperature. Amount of oxygen required to oxidise nitrite to nitrates is given by the relationship:

\[ UODN_i = 1.14 NO_2^– - N \]  

where: \( NO_2^– \) is the Nitrite – nitrogen concentration (mg/L) and \( UODN_i \) is the Ultimate oxygen demand for nitrite oxidation (mg/L)
The concentration of oxygen required to oxidize ammonia to nitrates is also obtained from the relationship:

\[ U_{ODN_{a}} = 4.57 A_{mm} - N \]  \hspace{1cm} (2)

where: \( U_{ODN_{a}} \) is the ultimate oxygen demand for ammonia-nitrogen oxidation (mg/L) and Amm-N is the ammonia-nitrogen concentration (mg/L)

Quantity of oxygen required to oxidize organic nitrogen is given by:

\[ U_{ODN} = 4.57 ON \]  \hspace{1cm} (3)

where: \( U_{ODN} \) is the ultimate oxygen demand for organic nitrogen oxidation (mg/L) and ON is the organic nitrogen concentration (mg/L)

Carbohydrates are oxidized under anaerobic conditions to yield carbon (IV) oxide and methane as follows:

\[
\begin{align*}
C_{n}H_{a}O_{b} & + \left( n - \frac{a}{4} - \frac{b}{2} \right) H_{2}O \\ & \rightarrow \left( \frac{n}{2} - \frac{a}{8} + \frac{b}{4} \right) CO_{2} + \left( \frac{n}{2} + \frac{a}{8} - \frac{b}{4} \right) CH_{4}
\end{align*}
\]  \hspace{1cm} (4)

Schroeder (1977) suggests the use of equation (4) to estimate the rate of methane production in respect of BOD concentration as follows

\[ M_{CH} = 0.35 \left( \eta Q C_{BOD} - 1.42 R \frac{V}{Q} \right) \]  \hspace{1cm} (5)

where: \( \eta \) is the conversion factor; \( C_{BOD} \) is the influent BOD (mg/L), \( M_{CH} \) is the methane produced per day (m³/d), \( Q \) is the discharge rate (m³/d) or volume of flow per unit time, \( R \) is the rate of bacterial growth (/d) and \( V \) is the volume of the liquid (m³).

Similarly, Tebbutt (1991) reports that carbohydrates are oxidized under aerobic conditions to yield carbon (IV) oxide and water as follows:

\[
\begin{align*}
C_{n}H_{a}O_{b} & \rightarrow (n) O_{2} \\
& \rightarrow (n) CO_{2} + (y) H_{2}O
\end{align*}
\]  \hspace{1cm} (6)

Concentration of oxygen required by microorganisms to oxidise carbohydrate in wastewater to water and carbon-(IV) oxide can be computed as follows:

\[ U_{OD_{2}} = 2.67 OC \]  \hspace{1cm} (7)

where: \( OC \) is the organic carbon concentration (mg/L); and \( U_{OD_{2}} \) is the ultimate oxygen demand for carbohydrate oxidation (mg/L).

In environmental pollution control, Biochemical Oxygen Demand kinetic parameters are used to
determine the approximate quantity of oxygen that will be required to stabilize organic matter present in the wastewater biologically; establish the critical point and the critical oxygen deficit in oxygen sag curve, which is applicable in the self-purification of streams (Metcalf and Eddy, 1991; Tebbutt, 1991; Viessman and Hammer, 1993); estimate the size of waste treatment plant required through the use of surface Biochemical Oxygen Demand loading (White, 1970, Fasanmi, 1994; Oke, 2001; Mahmood and Paice, 2006); design some biological treatment plants (ponds, lagoons, trickling bed filter, etc.); and measure efficacy of some biological treatment processes through the use of Biochemical Oxygen Demand concepts (Oke, 2001).

The key design parameters in BOD kinetics are ultimate Biochemical Oxygen Demand concentration (L₀) and rate of BOD concentration removal (k). Although there are various kinetics models for Biochemical Oxygen Demand removal (k), there are accepted and most widely used BOD concentration removal rate can be completed through the use of Biochemical Oxygen Demand first order kinetics model has been the widely accepted and most widely used BOD concentration kinetics order. Equation (8) presents Biochemical Oxygen Demand’s first order model and the kinetic parameters. There are several methods for the determination of these two essential design parameters (k and L₀) from a series of BOD concentration measured.

\[
Y_T = L_0 (1 - \exp^{-kt}) = L_0 (1 - 10^{-kt}) \quad (8)
\]

where: \( L_0 \) is the ultimate BOD concentration (mg/L), \( \exp \) is the exponential, \( k \) is the rate of Biochemical Oxygen Demand removal (/d) in base 10, \( k \) is the Biochemical Oxygen Demand removal rate at base e (/d) and \( t \) is the time of incubation (d).

The methods include non-linear regression method, least square, Lee’s and Moment methods, the logarithms difference, daily difference method, rapid-ratio method, Fujimoto and the Thomas method (Oke et al., 2009). The least squares method involves fitting curves through a set of data points into a linear equation so that the sum of the squares of the residuals must be the minimum. Using this method, a variety of different types of curves can be fitted to a linear equation and the key parameters can be determined. It is a simultaneous equation based on the function that can be expressed as follows (Oke et al., 2009):  

\[
\sum_{n=1}^{n} y^t = na + b \sum_{n=1}^{n} y \quad (9)
\]

\[
\sum_{n=1}^{n} y y^t = a \sum_{n=1}^{n} y + b \sum_{n=1}^{n} y^2 \quad (10)
\]

where: \( y \) is the Biochemical Oxygen Demand that has been exerted in the time interval \( t \) (mg/L) and \( y^t \) is the \( \left( \frac{y_{n+1} - y_n}{\Delta t} \right) \) \( k \) is the 'a' and \( L_0 \) is the value of 'b' divided by 'a'.

The logarithms difference method was developed in 1936 by Fair (Oke and Akindahunsi, 2005; Oke et al., 2009). The method requires the Biochemical Oxygen Demand to be observed at an equal interval for a period. Computation of the BOD concentration removal rate can be completed using the following equations (Oke et al., 2009):

\[
k = \frac{\sum_{n=1}^{n} \sum_{n=1}^{n} \log(d) - n \sum_{n=1}^{n} t \log d}{n \sum_{n=1}^{n} t^2 - \left( \sum_{n=1}^{n} t \right)^2} \quad (11)
\]

where: \( d \) is the successive difference in BOD concentration (mg/L) = BODᵢ - BODᵢ₋₁, \( n \) is the total number of samples. If the numbers of observations were equally spaced, equation (11) can be simplified to give:

\[
k = \frac{6}{n(n^2 - 1)} \left[ (n + 1) \sum_{n=1}^{n} \log d - 2 \sum_{n=1}^{n} t \log d \right] \quad (12)
\]

However, the ultimate BOD (L₀) for the set of BOD concentration can be determined using expression (Oke et al., 2009) given as:
In the two points method, computations of Biochemical Oxygen Demand constant and ultimate Biochemical Oxygen Demand are based on selection of two points from the Biochemical Oxygen Demand values at times 2t and t. From these two points, the ratio (∫) of Biochemical Oxygen Demand removal rate and ultimate Biochemical Oxygen Demand can be computed using the following equations (Oke et al., 2009):

\[
{\frac{y_{2t}}{y_t}} = \frac{L_o \left(10^{-b}\right)}{L_o \left(10^{-b}\right)} = r
\]  

(14)

\[
k = \frac{1}{t} \log \left(\frac{1}{r-1}\right)
\]  

(15)

\[
L_o = \frac{y_t}{2 - r}
\]  

(16)

The Thomas’ method for BOD kinetics determination is based on the similarity between two series functions stated in literature Thomas (1950); Metcalf and Eddy (1991). Detailed derivation of Thomas’ equation can be found in Metcalf and Eddy (1991); Oke, (2001); Oke et al., (2006; 2009). It is a graphical analysis based on the function as follows:

\[
\left(\frac{t}{y}\right)^\frac{1}{3} = (KL)^\frac{1}{3} + \frac{K^2}{6L_o^2} t
\]  

(17)

\[
\left(\frac{t}{y}\right)^\frac{1}{3}
\]  
is plotted as a function of \(t\), with the slope of the graph being \(\frac{K^2}{6L_o^2}\) and the intercept, \(KL_o^\frac{1}{3}\);

from which \(K\) and \(L\) are determined as follows: \(a = KL^\frac{1}{3}\); \(b = \frac{K^2}{L^\frac{2}{3}}; k = \frac{6b}{a}\) and \(L = \frac{1}{ka^3}\).

The Lee’s method is a graphical method, which involves iterations by plotting a series of graphs covering a range of BOD concentration based on the Phelp’s law. Also, a series of Biochemical Oxygen Demand (BOD) values are plotted against their corresponding time series, and a linear relation is obtained between the BOD and the time series by superimposing the time (t) on Lee’s grid on any linear distance in the proportion of the Phelp’s law.

In Fujimoto’s method (Fujimoto, 1964), an arithmetic plot is prepared from \(BOD_{r+1}\) (Equation 19) against BOD, (Equation 18). The value at the intersection of the plot with a line of slope 1 corresponds to the ultimate BOD. After the ultimate BOD has been determined, the removal rate of BOD is determined using Equation 18 or 19 and one of the BOD values.

\[
BOD_t = L_o \left(1 - e^{-kt}\right)
\]  

(18)

\[
BOD_{r+1} = L_o \left(1 - e^{-k(r+1)}\right)
\]  

(19)

In ratio (rapid ratio) method, an arithmetic plot is prepared from the ratio of \(BOD_{r+1}\) value to BOD, against \(BOD_{r+1}\) value. The value at the intersection of the plot with a line of slope 1 corresponds to the ultimate BOD value. After the ultimate BOD value has been determined, the rate of BOD removal is determined using Equation (18) and one of the BOD values.

Moment method was developed by Moore et al. (1950). The method involves fitting the BOD value with a first order curve that has its first two moments equal to those of the experimental BOD values. The values of \(L_o\) and \(k\) are determined from the following equations (Oke et al., 2009):

\[
\sum_{i=1}^{n} y_i = nL_o - L_o \sum_{i=1}^{n} \exp(-t_i)
\]  

(20)

\[
\sum_{i=1}^{n} y_i t_i = L_o \sum_{i=1}^{n} t_i - L_o \sum_{i=1}^{n} t_i \exp(-t_i)
\]  

(21)

From Equations 20 and 21, the values of \(n-\sum\exp(-t_i)\) and the \(\sum t_i - \sum t_i \exp(-t_i)\) are obtained from \(\sum y_i \) and the \(\sum t_i, y_i\) value of \(k\) can be determined from the two expressions. The value of \(L_o\) can be obtained using Equation (20) or Equation (21). Non-linear regression method is a computer and semi-logarithms graphical based method which can be used to determine these parameters as follows (Oke et al., 2006; 2009):

\[
\frac{y_{2t}}{y_t} = \frac{L_o \left(-\exp(-2t)\right)}{L_o \left(-\exp(-t)\right)} = R_x
\]  

(22)
The daily difference method is a graphical (Equation 25a) and linear regression (equations 25b and c) based method. It involves fitting curves through a set of BOD values into a linear equation so that the sum of the squares of the residuals must be a minimum. Using this method, a variety of different types of curves can be fitted to a linear equation and the key parameters would be determined. It is a simultaneous equation based on the function that can be expressed as follows (Oke et al., 2009):

\[
\frac{\Delta Y}{\Delta t} = L_o k \exp^{-kt} \tag{25a}
\]

\[
\sum_{n=1}^{n} \log_e \frac{\Delta Y}{\Delta t} = n \log_e L_o k - k \sum_{n=1}^{n} t \tag{25b}
\]

\[
\sum_{n=1}^{n} t \log_e \frac{\Delta Y}{\Delta t} = \log_e L_o k \sum_{n=1}^{n} t - k \sum_{n=1}^{n} t^2 \tag{25c}
\]

All these methods are limited in applications, accuracy, reliability and validity (some of the methods were either derived from a similar mathematical equation (estimation of points) or fitting curves into a linear equation). Orhon et al., (2000) describe the approach unjustifiable mathematically. Oke and Akindahunsi (2005), Gullermo et al. (1999), Oke et al., (2009) and other researchers studied evaluation of some of these methods without employing Microsoft Excel Solver method. Thus the need for statistical evaluation of Microsoft Excel Solver method is needed. The principal objective of this study is to use Microsoft Excel Solver and some of the commonly used methods for the determination of BOD value first order kinetics parameters and to present their statistical assessments.

**MATERIALS AND METHOD**

Wastewater samples were collected from the domestic -institutional waste stabilization ponds of the Obafemi Awolowo University, Ile-Ife, Nigeria twice in a month for three months (January to March 2013) and different days. The BOD values of the samples were determined for the first five days using Standard Methods as specified elsewhere (APHA, 2005; Oke and Akindahunsi, 2005; Oke et al., 2009). Calculations of the BOD kinetics parameters (ultimate BOD and rate of BOD removal) were conducted using Microsoft Excel Solver, non-linear regression, the least squares, Thomas, two points, Fujimoto, ratio and logarithms difference methods. Statistical assessments were conducted using Analysis of Variance (ANOVA), relative error, Akaike Information Criterion (AIC) and Model of Selection Criterion (MSC). The model of selection criterion (MSC) interprets the proportion of expected BOD (experimental BOD) variation that can be described by the calculated BOD values (BOD values from the methods). A higher value of MSC indicates higher accuracy, validity and right fit of the methods. The model of selection criterion was computed using equation (26) as follows:

\[
MSC = \ln \left( \frac{\sum_{i=1}^{n} (Y_{\text{expect}} - \bar{Y}_{\text{expect}})^2}{\sum_{i=1}^{n} (Y_{\text{expect}} - Y_{\text{cali}})^2} \right) - \frac{2p}{n} \tag{26}
\]

where: \(Y_{\text{expect}}\) is the BOD values from the experimental study; \(\bar{Y}_{\text{expect}}\) is the average BOD values from the experimental study; \(p\) is the total number of fixed parameters to be estimated in the methods; \(n\) is the total number of BOD values calculated, and \(Y_{\text{cali}}\) is the BOD value calculated using the methods.

**Akaike Information Criterion:** Information Criterion of Akaike (1976) allows a direct comparison of different methods with a different number of parameters (Romoe et al., 2002). It represents the information content of a given set of parameters by relating the coefficient of determination to the number of parameters that were required to establish the fit. The Akaike Information Criterion (AIC) was determined using the expression:

\[
AIC = N \left( \ln \sum_{i=1}^{n} (Y_{\text{expect}} - Y_{\text{cali}})^2 \right) + 2p \tag{27}
\]

where: \(p\) is the total number of fixed parameters to be computed in the methods; \(N\) is the total number of BOD concentration calculated.
Relative errors (RErr) were determined using Equation (28) as follows:

\[
RErr = \frac{\sum_{i=1}^{n} \left( \frac{Y_{\text{expecti}} - Y_{\text{cali}}}{Y_{\text{expecti}}} \right) \times 100}{N}
\]  

(28)

Sum of Square (SS), Mean Square (MS) and F-Value were computed as follows (Gardiner and Gettinby, 1998; Guttman, et al., 1971; Loveday, 1980):

\[
SSA = \left( E_{HA} \right)^2 - \frac{T_e^2}{N}
\]  

(29)

where: SSA is the sum of the square of factor A; \( T_e \) is the total effect of the factors, \( E_{HA} \) is the effect of factor A and N is the total number of BOD concentration.

\[
MSA = \frac{SSA}{N - 1}
\]  

(30)

where: MSA is the mean square of the factor and N-1 is the degree of freedom of the factor.

\[
F = \frac{MSA}{MSE}
\]  

(31)

where: MSE is the mean square of the error and F is the F-value.

Computations of ultimate BOD value and BOD removal rate were computed using Microsoft Excel Solver as follows Oke et al. 2016:

- Microsoft Excel Solver was added in on the toolbar of Microsoft Excel;
- Target (limit) value of the iteration was set for the software based on square of difference as

\[
\left( \sum_{i=1}^{n} BOD_i - L_o \sum_{i=1}^{n} \left( 1 - e^{-kt} \right) \right)^2 = 0;
\]

- Changing cells of the iterations were selected, number of iterations, degree of accuracy and maximum time for the iteration were set for the software to meet the target; and
- The iteration started through Microsoft Excel Solver (Figure 2).

RESULTS AND DISCUSSION

Biochemical Oxygen Demand curves for the wastewaters are as presented in Figure 3. Figure 4 shows BOD remaining curves for influent wastewaters. The curves show a typical lag time of less than a day. The curves revealed that the minimum BOD was 400 mg/L and the maximum was 1350 mg/L. These BOD values indicated that the wastewaters were active sewage (Mara, 2003).

A statistical evaluation of the BOD value (Table 1) revealed that there was a significant difference between the samples (\( F_{3,20} = 53.40407; p = 6.94 \times 10^{-10} \)) and the BOD consumed (\( F_{3,20} = 129.3497; p = 5.42 \times 10^{-14} \)) at 99% confidence level. From these figures, the BOD curves show a slight distinctive, three-phase profile, comprising an initial period of rapid oxygen uptake, a shoulder-like transition phase and then an extended period of slower oxygen uptake activity. This pattern was observed throughout the study period for all the BOD curves. This BOD value is the existence of similar patterns for carbonaceous BOD (Figure 5).

Individual BOD value and incubation time demonstrated a low degree of scattering or low noise, which could be attributed to the accuracy of the method (APHA, 2005) and the instrument. The three-phase profile indicates that there was a decrease in the rate of BOD concentration removal and the wastewaters were not homogenous in nature, rather the wastewaters were heterogenous in nature (Mara, 2003).
Open Microsoft Excel

Check under Data at the tool bar if Solver is available

Yes

At the toolbar click Microsoft logo, open Excel option and select add in. OK

No

Set the Target ($L$53), operation (minimization or value of zero) and changing cell($k$3: $k$7)

At Solver dialogue set the number of iterations and time. Click on Solver to solve

Target reached

No

Yes

End (Record the values)

Figure 2: Procedure for using Microsoft Excel Solver in the computation of BOD Kinetics Parameters
Figure 3: Pattern of BOD Removed from the Wastewater

Figure 4: Pattern of BOD Remaining in the Wastewater
The ultimate BOD from the BOD analysis using these selected methods are as presented in Table 2. The ultimate BOD ranged from 822 mg/L to 1813 mg/L. These values were similar to the ultimate BOD values documented in the literature for domestic wastewater. These wastewaters can be grouped as high domestic wastewaters (Metcalf and Eddy, 1991; Mara, 2003). A statistical analysis (Table 3) of the ultimate BOD shows that there was a significant difference between the methods ($F = 7.01319; p = 2.98 \times 10^{-9}$) at 99% confidence level. An evaluation of ultimate BOD revealed that there was a significant difference among the ultimate BOD values. This difference shows that the wastewaters were heterogeneous in composition. The differences were significant ($F_{5,45} = 31.99269; p = 9.35 \times 10^{-14}$) at 99% confidence level.

The values of the BOD removal rate (kinetic coefficients) for each assay determined by the eight different methods are as presented in Table 4. It can be understood that there are differences among the values of the constants calculated by the different methods with the kinetic coefficients ranging from -0.442 /d to -0.134 /d. These values were similar to the kinetic coefficients documented in the literature for untreated domestic wastewater (Mara, 2003). Again the wastewaters can be categorized as strong domestic wastewaters (Metcalf and Eddy, 1991; Mara, 2003). A statistical analysis (Table 5) of the kinetic coefficients showed that there was a significant difference between the methods ($F_{5,45} = 16.15646; p = 4.19 \times 10^{-9}$) $p < 0.01$. An evaluation of kinetic coefficients revealed that there was a difference between the kinetic coefficients. The differences were significant ($F_{5,45} = 9.04305; p = 1.22 \times 10^{-9}$) at 99% confidence level. This result indicated that there was a significant difference between the methods at 99% confidence level and that kinetic coefficients are a function of the method used.

The values of the ultimate BOD and kinetic coefficients for each assay determined by the
different methods presented in Tables 2 and 4 revealed that there were differences in the values of the ultimate BOD concentration and kinetic coefficients calculated by the different methods. However, a comparison by inspection does not give room to draw conclusions. Relative error, MSC and AIC were used to assess the degree of fit for each method (Tables 6 to 9). The relative error and the AIC are more common statistical evaluation techniques than the MSC. However, the model of selection criterion is not dependent on the numerical value of the measurements and places a burden on models with more parameters. MSC is, therefore, a more objective analysis of the degree of fit (Gullemo et al., 1999). The analysis of degree of fit was completed for each of the fitting methods and each curve is as presented in Tables 6 and 8.

From these results, it is clear that using the Microsoft Excel Solver method resulted (throughout) in the smallest relative error (0.62%), the lowest AIC (23.43) and the highest MSC (7.59). The non-linear regression method is the next to the Microsoft Excel Solver method. The non-linear regression method can be utilized on any electronic graphical systems, and most computer plotting packages and software have it built in too. Its drawback is that it gives a larger relative error (2.63%), a larger AIC (37.65) and a lower MSC (4.74) than Microsoft Excel Solver method due to the discrete estimation of the slope and ratio which were prepared at each point. The next method is the Thomas method (which is also easy to implement). The method originated from the similarity in shapes of an arbitrary function with that of the BOD curve, which is not always true. Its weakness is that it gives a larger relative error (3.48%), a larger AIC (42.34) and a lower MSC (3.80) than previously mentioned methods due to the discrete estimation of the slope which was done at each point. The next method after the Thomas’ method is the least squares method. The method can be applied on electronic devices, and most plotting packages have it built in too.

Table 2: Values of Ultimate BOD (mg/L) from all the Methods used

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>Sum of Squares</th>
<th>Degree of freedom</th>
<th>Mean Square</th>
<th>F Value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between BOD Concentration Removal rate</td>
<td>0.140446</td>
<td>5</td>
<td>0.02809</td>
<td>16.13646</td>
<td>4.19x 10^{-5}</td>
</tr>
<tr>
<td>Within the Methods Used</td>
<td>0.149115</td>
<td>9</td>
<td>0.01673</td>
<td>9.04505</td>
<td>1.22x 10^{-2}</td>
</tr>
<tr>
<td>Error</td>
<td>0.08247</td>
<td>45</td>
<td>0.001833</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>0.379672</td>
<td>59</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Values of Analysis of Variance of Ultimate BOD from all the Methods used

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>Sum of Squares</th>
<th>Degree of freedom</th>
<th>Mean Square</th>
<th>F Value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between Ultimate BOD Concentration</td>
<td>177944</td>
<td>5</td>
<td>35588.9</td>
<td>31.99269</td>
<td>9.35x 10^{-14}</td>
</tr>
<tr>
<td>Within the Methods Used</td>
<td>702138.6</td>
<td>9</td>
<td>78015.41</td>
<td>7.01319</td>
<td>2.98 x 10^{-6}</td>
</tr>
<tr>
<td>Error</td>
<td>50584.4</td>
<td>45</td>
<td>11124.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>2982172</td>
<td>59</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4: Values of BOD Removal Rate (/d) from all the Methods used

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>Sum of Squares</th>
<th>Degree of freedom</th>
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<td></td>
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<tr>
<td>Total</td>
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<td>59</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 6: Statistical Evaluation (Relative error, MSC and AIC) of all the Methods

<table>
<thead>
<tr>
<th>Method</th>
<th>MSC</th>
<th>AIC</th>
<th>Relative Error (%)</th>
<th>Relative Error (%)</th>
<th>Relative Error (%)</th>
<th>AIC</th>
<th>AIC</th>
<th>AIC</th>
<th>AIC</th>
<th>AIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microsoft Excel Solver</td>
<td>6.086</td>
<td>3.757</td>
<td>5.255</td>
<td>2.691</td>
<td>-1.946</td>
<td>-1.879</td>
<td>4.632</td>
<td>2.657</td>
<td>2.684</td>
<td>5.615</td>
</tr>
<tr>
<td>Least Squares</td>
<td>34.268</td>
<td>37.355</td>
<td>38.539</td>
<td>51.263</td>
<td>74.448</td>
<td>74.111</td>
<td>41.554</td>
<td>51.433</td>
<td>51.296</td>
<td>36.643</td>
</tr>
<tr>
<td>Thomas</td>
<td>46.571</td>
<td>14.411</td>
<td>3.255</td>
<td>2.691</td>
<td>-1.946</td>
<td>-1.879</td>
<td>4.632</td>
<td>2.657</td>
<td>2.684</td>
<td>5.615</td>
</tr>
<tr>
<td>Non-linear regression</td>
<td>52.576</td>
<td>53.351</td>
<td>51.263</td>
<td>74.448</td>
<td>74.111</td>
<td>41.554</td>
<td>51.433</td>
<td>51.296</td>
<td>36.643</td>
<td></td>
</tr>
<tr>
<td>Fujimoto</td>
<td>53.476</td>
<td>53.476</td>
<td>53.476</td>
<td>53.476</td>
<td>53.476</td>
<td>53.476</td>
<td>53.476</td>
<td>53.476</td>
<td>53.476</td>
<td></td>
</tr>
<tr>
<td>Ratio</td>
<td>41.554</td>
<td>51.433</td>
<td>51.296</td>
<td>36.643</td>
<td>74.111</td>
<td>74.111</td>
<td>41.554</td>
<td>51.433</td>
<td>51.296</td>
<td>36.643</td>
</tr>
<tr>
<td>Logarithms difference</td>
<td>4.632</td>
<td>2.657</td>
<td>2.684</td>
<td>5.615</td>
<td>41.554</td>
<td>41.554</td>
<td>51.433</td>
<td>51.296</td>
<td>36.643</td>
<td></td>
</tr>
<tr>
<td>Two Points</td>
<td>2.657</td>
<td>2.684</td>
<td>5.615</td>
<td>41.554</td>
<td>41.554</td>
<td>41.554</td>
<td>51.433</td>
<td>51.296</td>
<td>36.643</td>
<td></td>
</tr>
<tr>
<td>Daily Difference</td>
<td>2.657</td>
<td>2.684</td>
<td>5.615</td>
<td>41.554</td>
<td>41.554</td>
<td>41.554</td>
<td>51.433</td>
<td>51.296</td>
<td>36.643</td>
<td></td>
</tr>
<tr>
<td>Moore et al. (1950)</td>
<td>2.657</td>
<td>2.684</td>
<td>5.615</td>
<td>41.554</td>
<td>41.554</td>
<td>41.554</td>
<td>51.433</td>
<td>51.296</td>
<td>36.643</td>
<td></td>
</tr>
</tbody>
</table>

Table 7: ANOVA the Statistical Evaluation (Relative error, MSC and AIC) of all the Methods

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>Sum of Squares</th>
<th>Degree of freedom</th>
<th>Mean Square</th>
<th>F-value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Within Statistical Evaluation Method</td>
<td>69429.03</td>
<td>17</td>
<td>4084.061</td>
<td>30.7525</td>
<td>9.54x 10^-4</td>
</tr>
<tr>
<td>Between BOD Kinetics Methods</td>
<td>10725.41</td>
<td>9</td>
<td>1191.712</td>
<td>8.97345</td>
<td>8.15x 10^-11</td>
</tr>
<tr>
<td>Error</td>
<td>20319.04</td>
<td>153</td>
<td>132.8042</td>
<td>79.85</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100473.5</td>
<td>179</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 8: Summary of the Statistical Evaluation (Relative error, MSC and AIC) of all the Methods

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MSC</td>
<td>7.39</td>
<td>3.47</td>
<td>3.80</td>
<td>4.74</td>
<td>-0.91</td>
<td>-0.84</td>
<td>2.48</td>
<td>1.76</td>
<td>1.37</td>
<td>3.46</td>
</tr>
<tr>
<td>AIC</td>
<td>23.43</td>
<td>44.01</td>
<td>42.34</td>
<td>37.65</td>
<td>65.90</td>
<td>63.55</td>
<td>48.97</td>
<td>52.55</td>
<td>54.49</td>
<td>44.08</td>
</tr>
<tr>
<td>Relative Error (%)</td>
<td>0.62</td>
<td>3.50</td>
<td>3.48</td>
<td>2.63</td>
<td>39.53</td>
<td>38.86</td>
<td>16.46</td>
<td>15.83</td>
<td>21.95</td>
<td>4.08</td>
</tr>
</tbody>
</table>

Table 9: ANOVA of Summary of the Statistical Evaluation of all the Methods

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>Sum of Squares</th>
<th>Degree of freedom</th>
<th>Mean Square</th>
<th>F-value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Within Statistical Evaluation Method</td>
<td>10965.75</td>
<td>2</td>
<td>5482.877</td>
<td>58.07803</td>
<td>0.141 x 10^-8</td>
</tr>
<tr>
<td>Between BOD Kinetics Methods</td>
<td>17907.33</td>
<td>9</td>
<td>198.9703</td>
<td>2.107617</td>
<td>0.085192</td>
</tr>
<tr>
<td>Error</td>
<td>1699.296</td>
<td>18</td>
<td>94.40536</td>
<td>79.85</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>14455.78</td>
<td>29</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Its drawback is that it gives a larger relative error (3.50 %), a larger AIC (44.01) and a lower MSC (3.47) than Microsoft Excel Solver and non-linear regression methods due to the discrete estimation of the slope which was conducted at each point. The next method is the Moore et al. (1950) method (which is also easy to implement). The method originated from the similarity in shapes of an arbitrary function with that of the BOD curve. Its hindrance is that it gives a larger relative error (4.08 %), a larger AIC (44.08) and a lower MSC (3.46) than previously mentioned methods due to the detail in the estimation of the slope which was prepared at each point.
The other methods had their relative error greater than 5.0%. The daily difference, two points, logarithms difference, Fujimoto and ratio methods had a relative error of 21.95%; 15.83%; 16.46%; 39.53 and 38.86% respectively. The MSC values of these methods were 1.37; 1.76; 2.48; -0.91 and -0.84 respectively. The AIC values for these selected methods were 54.49, 52.55, 48.97; 65.90 and 65.55 respectively. These high values of relative errors, AIC and MSC indicate that the accuracies of these methods were lower than expected, which makes them not applicable in environmental engineering (error > 5%). Although it can be disputed that Microsoft Excel Solver and non-linear methods are harder to implement, the extended use of computers (high speed with relatively high capacity and high read only memory (ROM)) and the existence of information technology packages or routines for non-linear parameter estimation have made its implementation much simpler. Therefore, Microsoft Excel Solver should be the method of choice in the determination of first order kinetics parameter of BOD.

CONCLUSION
The study utilised Microsoft Excel Solver for Biochemical Oxygen Demand (BOD) first order kinetics toward error free kinetics parameters determination. It can be concluded that Microsoft Excel Solver is the best method for estimating first order kinetics parameters of BOD Concentration; non-linear regression, least squares, and Thomas methods should be employed as an alternative to Microsoft Excel Solver for BOD kinetic parameters determination; there is the need to provide a better solution to some of these methods such as daily difference, ratio, logarithms difference, Moore et al. (1950) and other models with higher relative error greater than 5%; and there is the need to evaluate other BOD kinetics models (methods) and conduct their statistical evaluations.

REFERENCES
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Liu, J., Olsson, G. and Mattiasson, B. 2004. Short-


White, J.B. 1970. The design of sewers and sewage Treatment works, 1st edn, Edward Arnold Publisher Ltd, London.