

## AN IMPROVED SOLUTION OF FIRST ORDER KINETICS FOR BIOCHEMICAL OXYGEN DEMAND

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### 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:

$$UODN_i = 1.14NO_2 - N \quad (1)$$

where:  $NO_2 - N$  is the Nitrite – nitrogen concentration (mg/L) and  $UODN_i$  is the Ultimate oxygen demand for nitrite oxidation (mg/L)

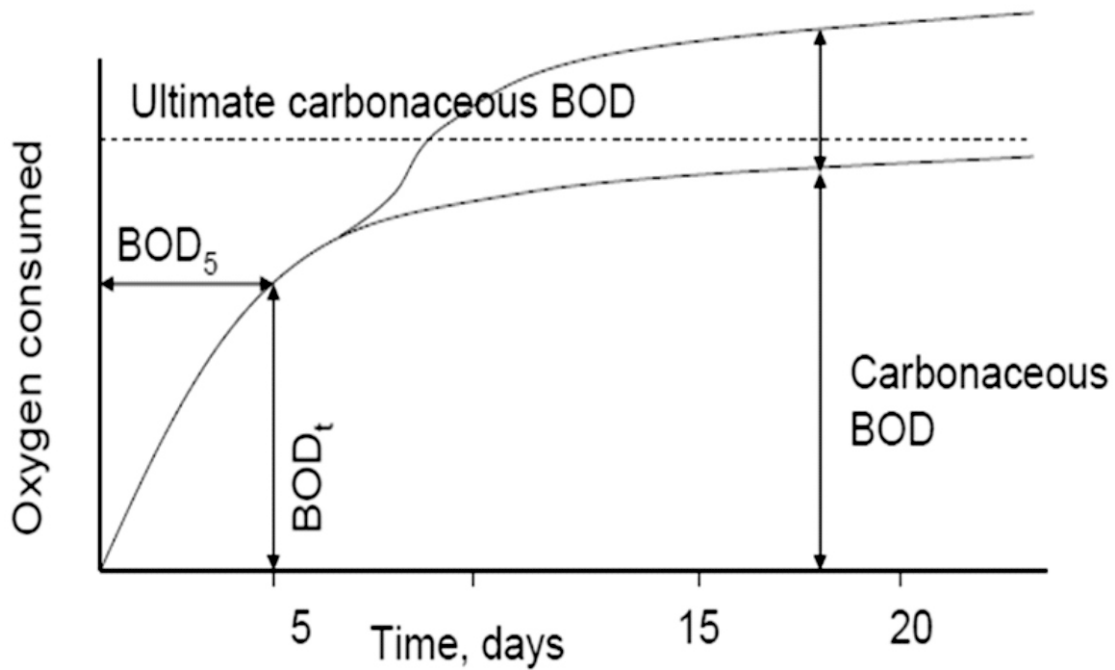


Figure 1: Pattern of First Order Kinetics of Carbonaceous and Nitrogenous Biochemical Oxygen Demand (Tebbutt, 1991)

The concentration of oxygen required to oxidize ammonia to nitrates is also obtained from the relationship:

$$UODN_{ia} = 4.57Amm - N \quad (2)$$

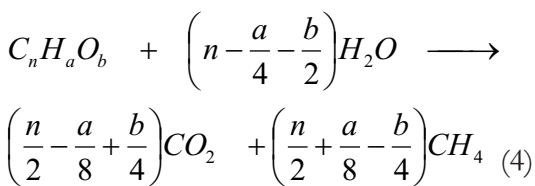
where:  $UODN_{ia}$  is the ultimate oxygen demand for ammonia- nitrogen oxidation (mg/L) and  $Amm-N$  is the ammonia - nitrogen concentration (mg/L)

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

$$UODN = 4.57ON \quad (3)$$

where:  $UODN$  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:



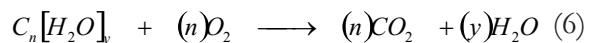
Schroeder (1977) suggests the use of equation (4)

to estimate the rate of methane production in respect of BOD concentration as follows

$$M_{CH} = 0.35(\eta QC_{BODi} - 1.42R_g V) \quad (5)$$

where:  $\eta$  is the conversion factor;  $C_{BODi}$  is the influent BOD (mg/L),  $M_{CH}$  is the methane produced per day ( $m^3/d$ ),  $Q$  is the discharge rate ( $m^3/d$ ) or volume of flow per unit time,  $R_g$  is the rate of bacterial growth (/d) and  $V$  is the volume of the liquid ( $m^3$ ).

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



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

$$UOD_L = 2.67OC \quad (7)$$

where:  $OC$  is the organic carbon concentration (mg/L); and  $UOD_L$  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 ( $L_o$ ) and rate of BOD concentration removal ( $k$ ). Although, there are various kinetics models for Biochemical Oxygen Demand removal rate in the literature (Moore *et al.*, 1950; Thomas, 1950; Navone, 1960; Sheehy, 1960; Fujimoto, 1964; Weber and Carlson, 1965; Young and Clark, 1965; Keshavan *et al.*, 1965; Marske and Polkowsky, 1972; Hewitt and Hunter, 1975; Hewitt *et al.*, 1979; Swamee and Ojha, 1991; Adrian and Sander, 1993; Sohn *et al.*, 1995; Reynolds and Ahmad, 1997; Adrian and Sander, 1998; Borsuk and Stow, 2000; Liu *et al.*, 2004; Mason *et al.*, 2006; Siwec *et al.*, 2011; 2012; Kalambar *et al.*, 2014; Srinvasa Rao *et al.*, 2015), 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  $L_o$ ) from a series of BOD concentration measured.

$$Y_t = L_o(1 - EXP^{-kt}) = L_o(1 - 10^{-k't}) \quad (8)$$

where:  $L_o$  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):

$$\sum_{n=1}^n y' = na + b \sum_{n=1}^n y \quad (9)$$

$$\sum_{n=1}^n yy' = a \sum_{n=1}^n y + b \sum_{n=1}^n y^2 \quad (10)$$

where:  $y$  is the Biochemical Oxygen Demand that has been exerted in the time interval  $t$  (mg/L) and

$y'$  is the  $\left(\frac{y_{n+1} - y_{n-1}}{\Delta t}\right)$   $k$  is the 'a' and  $L_o$  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):

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

where:  $d$  is the successive difference in BOD concentration (mg/L) =  $BOD_t - BOD_{t+1}$ ,  $n$  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 ( $L_o$ ) for the set of BOD concentration can be determined using expression (Oke *et al.*, 2009) given as:

$$L_o = \frac{(1-10^{-k})(1-10^{-kt})y_t}{n(1-10^{-k}) - 2x10^{-k}(1-10^{-nk}) + 10^{-2nk}(1-10^{-2nk})} \quad (13)$$

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 ( $r$ ) of Biochemical Oxygen Demand removal rate and ultimate Biochemical Oxygen Demand can be computed using the following equations (Oke *et al.*, 2009):

$$\frac{y_{2t}}{y_t} = \frac{L_o(1-10^{-2kt})}{L_o(1-10^{-kt})} = r \quad (14)$$

$$k = \frac{1}{t} \log\left(\frac{1}{r-1}\right) \quad (15)$$

$$L_o = \frac{y_t}{2-r} \quad (16)$$

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:

$$\left(\frac{t}{y}\right)^{\frac{1}{3}} = (KL)^{-\frac{1}{3}} + \frac{K^{\frac{2}{3}}}{6L_o^{\frac{1}{3}}}t \quad (17)$$

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

from which  $K$  and  $L$  are determined as follows:  $a =$

$$KL_o^{-\frac{1}{3}}; b = \frac{K^{\frac{2}{3}}}{6L_o^{\frac{1}{3}}}; k = \frac{6b}{a} \text{ and } L = \frac{1}{ka^3}$$

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  $BOD_{t+1}$  (Equation 19) against  $BOD_t$  (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.

$$BOD_t = L_o(1 - e^{-kt}) \quad (18)$$

$$BOD_{t+1} = L_o(1 - e^{-k(t+1)}) \quad (19)$$

In ratio (rapid ratio) method, an arithmetic plot is prepared from the ratio of  $BOD_{t+1}$  value to  $BOD_t$  against  $BOD_{t+1}$  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):

$$\sum_{i=1}^n y_i = nL_o - L_o \sum_{i=1}^n \exp^{-kt_i} \quad (20)$$

$$\sum_{i=1}^n y_i t_i = L_o \sum_{i=1}^n t_i - L_o \sum_{i=1}^n t_i \exp^{-kt_i} \quad (21)$$

From Equations 20 and 21, the values of

$$\frac{n - \sum_{i=1}^n \exp^{-kt_i}}{\sum_{i=1}^n y_i} \text{ are obtained from } \frac{\sum_{i=1}^n y_i}{\sum_{i=1}^n t_i y_i} \text{ and the}$$

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):

$$\frac{y_{2t}}{y_t} = \frac{L_o(1 - \text{Exp}^{-2kt})}{L_o(1 - \text{Exp}^{-kt})} = R_e \quad (22)$$



$$k = \frac{1}{t} \ln \left( \frac{1}{R_e - 1} \right) \quad (23)$$

$$L_o = \frac{y_t}{2 - R_e} \quad (24)$$

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):

$$\frac{\Delta y}{\Delta t} = L_o k \exp^{-kt} \quad (25a)$$

$$\sum_{n=1}^n \text{Log}_e \frac{\Delta y}{\Delta t} = n \text{Log}_e L_o k - k \sum_{n=1}^n t \quad (25b)$$

$$\sum_{n=1}^n t \text{Log}_e \frac{\Delta y}{\Delta t} = \text{Log}_e L_o k \sum_{n=1}^n t - k \sum_{n=1}^n t^2 \quad (25c)$$

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), Gullemo *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:

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

where:  $Y_{\text{expecti}}$  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:

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

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:

$$RErr = \frac{\sum_{i=1}^N \left( 100 \left( \frac{Y_{expecti} - Y_{cali}}{Y_{expecti}} \right) \right)}{N} \quad (28)$$

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

$$SSA = (E_{HA_s})^2 - \frac{T_e^2}{N} \quad (29)$$

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

$$MSA = \frac{SSA}{N-1} \quad (30)$$

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

$$F = \frac{MSA}{MSE} \quad (31)$$

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

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

- 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 ( $F_{5,20} = 53.40407$ ;  $p = 6.94 \times 10^{-11}$ ) and the BOD consumed ( $F_{4,20} = 129.3497$ ;  $p = 5.42 \times 10^{-14}$ ) 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).

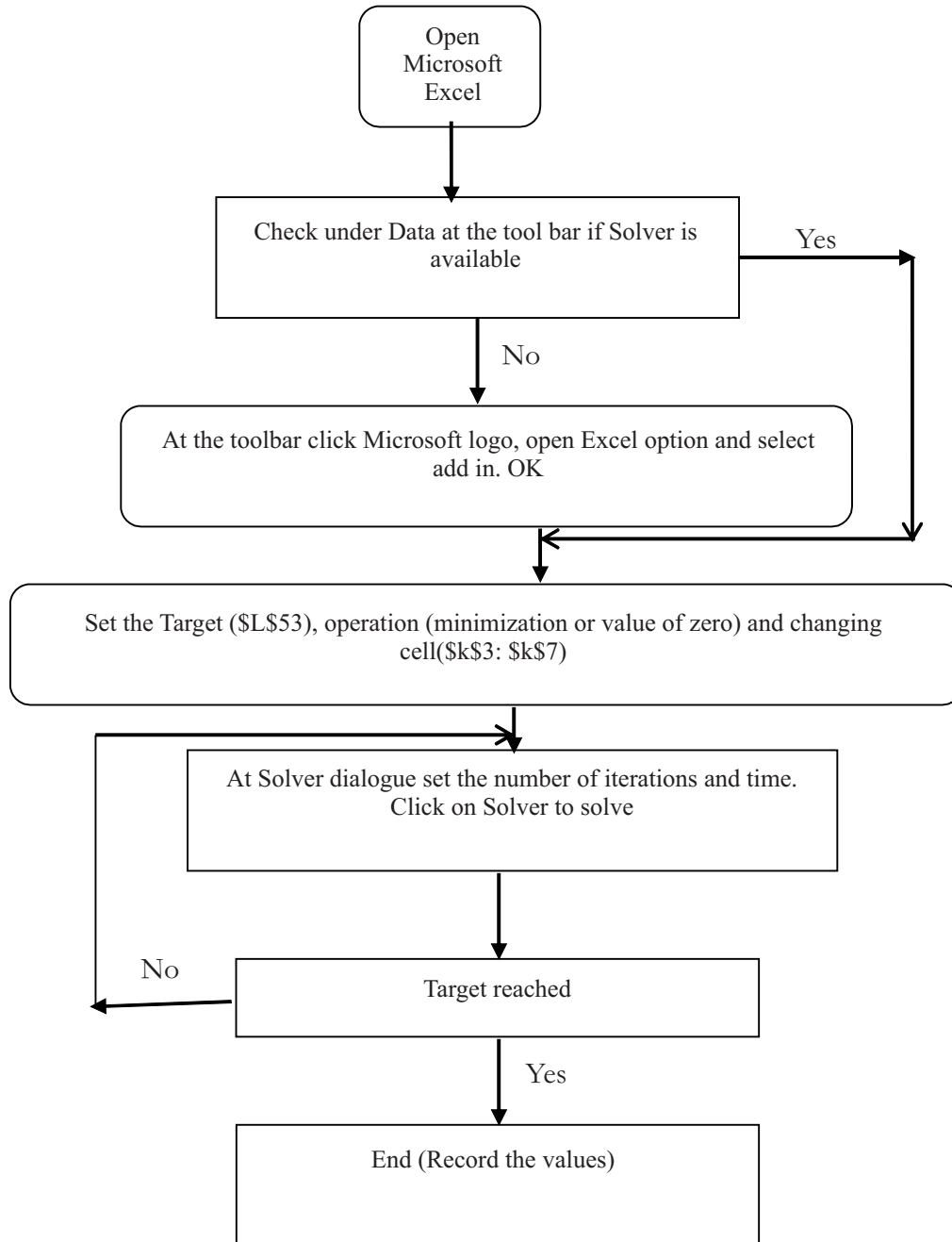


Figure 2: Procedure for using Microsoft Excel Solver in the computation of BOD Kinetics Parameters

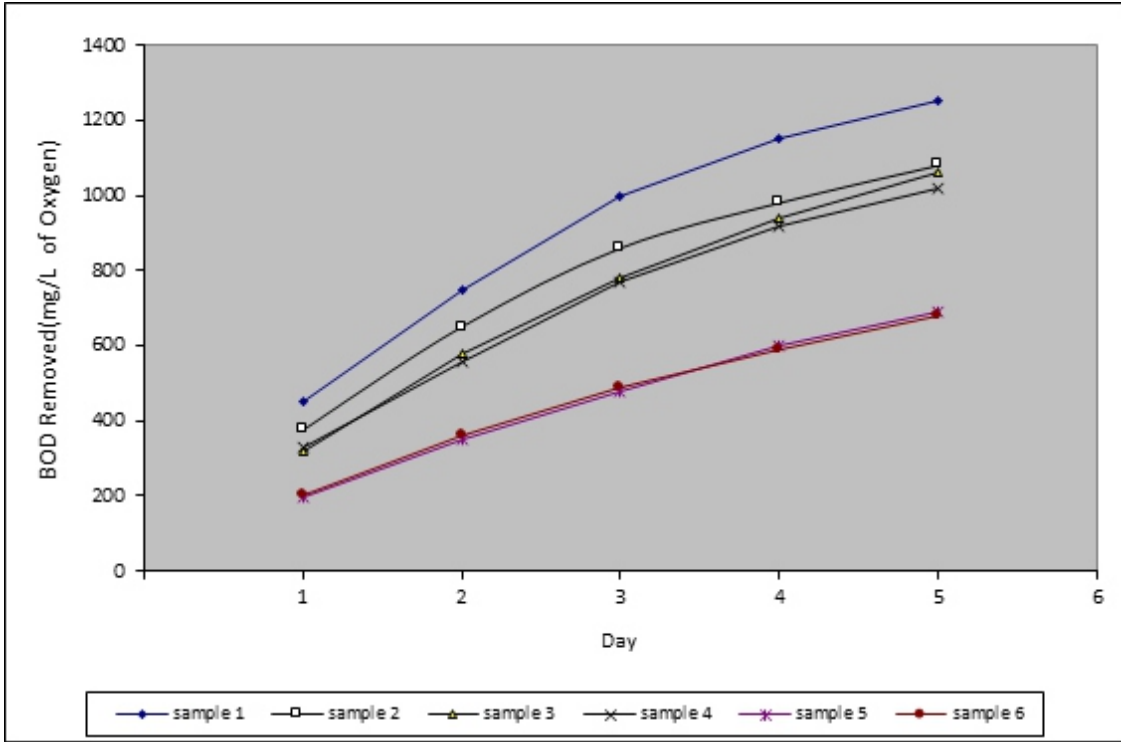


Figure 3: Pattern of BOD Removed from the Wastewater

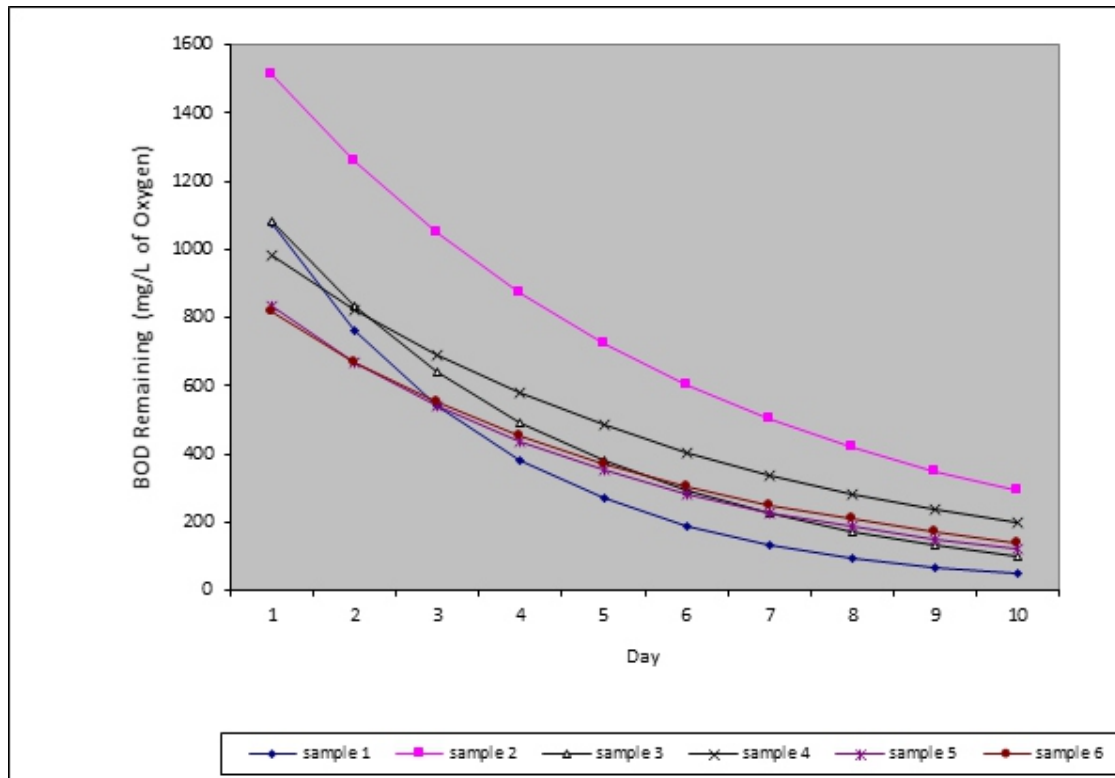


Figure 4: Pattern of BOD Remaining in the Wastewater



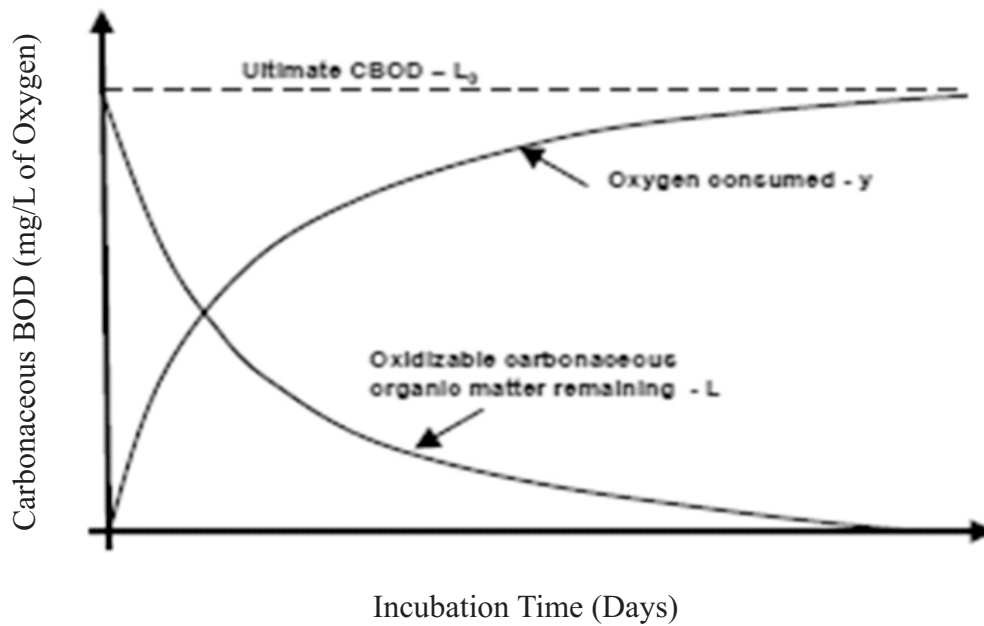


Figure 5: Pattern of Carbonaceous BOD in First Order Kinetics (Source: Thomann and Mueller, 1987)

Table 1: The Analysis of Variance of Carbonaceous BOD

Source of Variation	Sum of Squares	Degree of freedom	Mean Square	F- Value	P-value
Between the samples	839690	5	167938	53.40407	$6.94 \times 10^{-11}$
Within the BOD					
Consumed	1627047	4	406761.7	129.3497	$5.42 \times 10^{-14}$
Error	62893.33	20	3144.667		
Total	2529630	29			

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 ( $F_{9,45} = 7.01319$ ;  $p = 2.98 \times 10^{-6}$ ) 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 ( $F_{9,45} = 16.15646$ ;  $p = 4.19 \times 10^{-9}$ )  $p < 0.01$ . An evaluation of kinetic coefficients revealed that there was a difference between the kinetic coefficients. The differences were significant ( $F_{5,45} = 9.04305$ ;  $p = 1.22 \times 10^{-7}$ ) 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

Microsoft Excel Solver	Least Squares	Thomas	Non-linear regression	Fujimoto	Ratio	Logarithms difference	Two Points	Daily Difference	Moore et al. (1950)
1525	1507	1489	1458	1125	1365	1442	1350	1419	1517
1813	1391	1333	1474	1061	1205	1369	1406	1307	1330
1404	1606	1320	1568	1069	1257	1556	1707	1495	1522
1173	1458	1370	1221	1052	1209	1376	1089	1334	1386
1029	1256	1135	1172	879	859	1161	951	1126	1160
991	1115	1061	989	859	822	1064	1000	1028	1039

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

Source of Variation	Sum of Squares	Degree of freedom	Mean Square	F- Value	P-value
Between Ultimate BOD Concentration	1779449	5	355889.9	31.99269	9.35x 10 <sup>-14</sup>
Within the Methods Used	702138.6	9	78015.41	7.01319	2.98 x 10 <sup>-6</sup>
Error	500584.4	45	11124.1		
Total	2982172	59			

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

Microsoft Excel Solver	Least Squares	Thomas	Non-linear regression	Fujimoto	Ratio	Logarithms difference	Two Points	Daily Difference	Moore et al. (1950)
-0.348	-0.350	-0.357	-0.342	-0.166	-0.135	-0.394	-0.405	-0.442	-0.346
-0.184	-0.252	-0.261	-0.235	-0.159	-0.139	-0.305	-0.310	-0.392	-0.263
-0.262	-0.226	-0.279	-0.232	-0.166	-0.140	-0.231	-0.207	-0.261	-0.240
-0.178	-0.144	-0.158	-0.170	-0.157	-0.135	-0.272	-0.361	-0.308	-0.156
-0.215	-0.173	-0.192	-0.186	-0.135	-0.139	-0.182	-0.229	-0.196	-0.186
-0.196	-0.172	-0.182	-0.197	-0.134	-0.140	-0.207	-0.223	-0.227	-0.197

Table 5: Values of Analysis of Variance of BOD Removal Rate from all the Methods used

Source of Variation	Sum of Squares	Degree of freedom	Mean Square	F- Value	P-value
Between BOD Concentration Removal rate	0.148046	5	0.029609	16.15646	4.19x 10 <sup>-9</sup>
Within the Methods Used	0.149155	9	0.016573	9.04305	1.22x 10 <sup>-7</sup>
Error	0.08247	45	0.001833		
Total	0.379672	59			

Table 6: Statistical Evaluation (Relative error, MSC and AIC) of all the Methods

	Microsoft Excel Solver	Least Squares	Thomas	Non-linear regression	Fujimoto	Ratio	Logarithms difference	Two Points	Daily Difference	Moore et al (1950)
MSC	6.086	5.472	5.235	2.691	-1.946	-1.879	4.632	2.657	2.684	5.615
AIC	34.288	37.355	38.539	51.263	74.448	74.111	41.554	51.433	51.296	36.643
Relative Error (%)	0.917	1.220	1.307	5.236	55.309	53.999	2.102	3.464	6.277	1.148
MSC	8.378	2.582	2.049	3.144	-1.358	-1.296	2.724	1.984	0.980	2.093
AIC	22.465	51.450	54.114	48.636	71.147	70.838	50.739	54.437	59.460	53.892
Relative Error (%)	0.513	4.754	6.073	3.666	47.453	46.439	8.543	11.878	19.686	5.961
MSC	7.244	2.449	2.261	6.115	0.557	0.823	-1.643	-1.159	-1.858	2.189
AIC	23.543	47.517	48.455	29.189	56.974	55.645	67.978	65.557	69.052	48.815
Relative Error (%)	0.778	5.148	6.535	1.157	18.882	17.279	58.666	49.964	66.720	6.724
MSC	8.115	2.776	4.377	3.653	-1.035	-1.038	5.168	3.566	4.037	4.271
AIC	18.801	45.499	37.495	41.114	64.552	64.566	33.536	41.547	39.191	38.022
Relative Error (%)	0.332	3.868	1.788	2.531	40.295	40.268	1.832	3.425	2.154	1.876
MSC	8.109	4.072	5.099	8.103	-0.756	-0.798	1.506	1.757	1.022	3.114
AIC	18.032	38.217	33.082	18.059	62.356	62.564	51.046	49.792	53.465	43.007
Relative Error (%)	0.575	2.493	1.677	0.578	35.731	36.297	11.145	10.408	14.918	4.687
MSC	6.052	3.020	4.084	3.378	-1.374	-1.287	3.951	2.735	2.503	3.931
AIC	32.967	48.127	42.805	46.337	70.095	69.660	43.467	49.552	50.712	43.572
Relative Error (%)	1.254	3.797	2.481	3.252	45.250	43.904	2.552	4.309	6.027	2.567

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

Source of Variation	Sum of Squares	Degree of freedom	Mean Square	F- Value	P-value
Within Statistical Evaluation Method	69429.03	17	4084.061	30.7525	9.54x 10 <sup>-41</sup>
Between BOD Kinetics Methods	10725.41	9	1191.712	8.97345	8.15x 10 <sup>-11</sup>
Error	20319.04	153	132.8042		
Total	100473.5	179			

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

Averages	Microsoft Excel Solver	Least Squares	Thomas	Non-linear regression	Fujimoto	Ratio	Logarithms difference	Two Points	Daily Difference	Moore et al (1950)
MSC	7.59	3.47	3.80	4.74	-0.91	-0.84	2.48	1.76	1.37	3.46
AIC	23.43	44.01	42.34	37.65	65.90	65.55	48.97	52.55	54.49	44.08
Relative Error (%)	0.62	3.50	3.48	2.63	39.53	38.86	16.46	15.83	21.95	4.08

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

Source of Variation	Sum of Squares	Degree of freedom	Mean Square	F- Value	P-value
Within Statistical Evaluation Method	10965.75	2	5482.877	58.07803	1.41 x 10 <sup>-8</sup>
Between BOD Kinetics Methods	1790.733	9	198.9703	2.107617	0.085192
Error	1699.296	18	94.40536		
Total	14455.78	29			

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. 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 Solve 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.

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