NEWTON RAPHSON SOLUTIONS OF BIOCHEMICAL OXYGEN DEMAND (BOD) KINETICS

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ABSTRACT
This paper evaluated Newton-Raphson method (NRM) solutions of Biochemical Oxygen Demand (BOD) kinetics with the aim of ascertaining error free solutions. Non-linear regression, logarithms difference, NRM, least square, daily difference, Thomas, two points, ratio and Fujimoto methods were used to determine constants in BOD kinetics. Microsoft Excel was employed in all methods used to solve the problems. Accuracies of all the methods were evaluated using relative error, Coefficient of Determination (CD), reliability and Model of Selection Criterion (MSC). The study revealed that the values of ultimate BOD and BOD removal rates were in the range of 859 to 1911 mg/l and -0.140/d to -0.449 /d respectively. Average total error for the methods were 23.85, 25.7, 74.72, 88.68, 1066.5, 1016.33, 149.12, 78.1 and (61.45 and 59.10) for non-linear regression, logarithms difference, least squares, Thomas, Fujimoto, Ratio, two points, daily difference and NRM (matrix and graphical).
Accuracy, validity and good fitness of these methods were in order of non-linear regression (8.16) > Logarithm difference (7.72) > NRM (6.26) > least square (6.03) > daily difference (5.42) > Thomas (5.04) > two points (4.14) > ratio (0.63) and Fujimoto (0.51) on basis of their average MSC values. It was concluded that NRM could be used for BOD kinetics. NRM is a better option because of its simplicity and flexibility as a graphical and numerical solution method.

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1.0 INTRODUCTION
It has been well documented that wastewater treatment processes are significant tools in environmental pollution control. These processes can be physical, chemical, irradiation, electrical, membrane and biological treatment processes. Biological treatment processes utilization for the treatment of domestic and industrial wastewaters has increased immensely. The processes have been found to be appropriate technologies for nations where land and labour are still relatively cheap and the climate support natural biodegrading operations (Mahmood and Paice, 2006). These treatment processes are common in Asia, Latin America and Africa continents (Hodgson, 2000). Waste stabilization ponds are typical biological treatment processes that have been installed in some of the industrial estates and institutions in Nigeria (Ogunfowokan et al., 2005). In addition, septic tanks and soak away system are the other forms of biological treatment process in almost every household and offices in Nigeria. In the
design and construction of these biological treatment systems the knowledge of ultimate Biochemical Oxygen Demand (\(I_{\text{u}}\)), the rates of carbonaceous deoxygenation (\(k\)) and nitrification are the basic tools. Figure 1 presents the common Biochemical Oxygen Demand (BOD). It has been reported that BOD concentration (\(\text{BOD}_c\)) and BOD kinetics are the most widely used parameters for organic pollution control and the determination of strength of wastewaters (Oke et al., 2018). BOD\(_c\) is a measure of the dissolved oxygen used by microorganisms in the biochemical oxidation of organic matters. BOD\(_c\) can be in the form of Carbonaceous Biochemical Oxygen Demand (CBOD) or Nitrogenous Biochemical Oxygen Demand (NBOD). These two types BOD\(_c\) are expressed as follows (Oke et al., 2018): Amount of oxygen required to oxidize nitrite to nitrate can be expressed as presented in equation (1):

\[
UO\text{D}_{\text{N}_2} = 1.14 \times \text{NO}_2 - N
\]

(1)

Where; NO\(_2\) - N is the Nitrite – nitrogen concentration (mg/l) and UOD\(_N\) is the Ultimate oxygen demand for nitrite oxidation (mg/l)

The amount of oxygen concentration required to transform (oxidize) ammonia to nitrate is estimated as follows (equation (2)):

\[
UO\text{D}_{\text{N}} = 4.57 \times \text{Amm} - N
\]

(2)

Where: UOD\(_N\) is the ultimate oxygen demand for ammonia- nitrogen oxidation (mg/l) and Amm-N is the ammonia - nitrogen concentration (mg/l)

The amount of oxygen concentration required to remove (oxidize) organic nitrogen can be computed as follows (equation (3)):

\[
UO\text{D}_O = 4.57 \times \text{ON}
\]

(3)

Where: UOD\(_S\) is the ultimate oxygen demand for organic nitrogen oxidation (mg/l) and ON is the organic nitrogen concentration (mg/l)

Carbohydrates are transformed (oxidized) under anaerobic conditions to yield carbon (IV) oxide and methane as follows (equation (4)):

\[
C_n\text{H}_m\text{O}_l + \left(\frac{n-a}{4} - \frac{b}{2}\right)\text{H}_2\text{O} \rightarrow \left(\frac{n-a}{8} + \frac{b}{4}\right)\text{CO}_2
\]

\[
+ \left(\frac{n-2}{4}\right)\text{CH}_4
\]

(4a)

Aerobic:

\[
C_n\text{H}_m\text{O}_l + \left(\frac{n-a}{4} - \frac{b}{2}\right)\text{O}_2 \rightarrow \left(\frac{n-a}{4} + \frac{b}{2}\right)\text{CO}_2
\]

\[
+ \left(\frac{a}{4} + \frac{b}{2}\right)\text{H}_2\text{O} + \text{Energy}
\]

(4b)

Schroeder (1977) and Oke et al. (2018) suggest the use of equation (4) to estimate the rate of methane production as follows (equation (5)):

\[
M_{\text{CH}_4} = 0.35\left(\eta QC_{\text{BOD}} - 1.42R_{S}\dot{V}\right)
\]

(5)

Where: \(\eta\) is the constant as multiplication factor; \(C_{\text{BOD}}\) is the influent BOD\(_c\) (mg/l), \(M_{\text{CH}_4}\) is the methane produced per day (m\(^3\)/d), \(Q\) is the discharge or flow rate (m\(^3\)/d), \(R_{s}\) is the rate of bacterial growth (/d) and \(\dot{V}\) is the volume of the liquid (m\(^3\)).

Tebbutt (1991) and Oke et al. (2018) report that carbohydrates are oxidized under aerobic conditions to yield carbon (IV) oxide and water as

\[
C_n\text{H}_m\text{O}_l + \left(n\right)\text{O}_2 \rightarrow \left(n\right)\text{CO}_2 + \left(y\right)\text{H}_2\text{O}
\]

(6)

follows:

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

\[
UO\text{D}_O = 2.67 \times \text{OC}
\]

(7)

Figure 1: Pattern of First Order Kinetics of Carbonaceous and Nitrogenous BOD Concentration. Source: Oke et al., 2018
Where: OC is the organic carbon or volatile solids concentration (mg/l) and UOD\textsubscript{c} is the ultimate oxygen demand for carbohydrate oxidation (mg/l).

The methods for the determination of these essential parameters are the Thomas' method, the Fujimoto method, the rapid ratio method and the moment's method, the logarithms difference method, the Newton Raphson method, the Lees' graphical methods, non-linear regression (Oke et al., 2018), the least squares method and daily difference method (Oke et al., 2018). More on BOD\textsubscript{c}, BOD kinetics and all these methods can be found in 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), Adraian and Sanders (1993, 1998), Fasanmi (1994), Sohn et al. (1995), Reynolds and Ahmad (1997), Borsuk and Stow (2000), Hodgson (2000), Gullermo et al. (2000), Mara (2003), Liu et al. (2004), Ian et al. (2006), Mason et al. (2006), Siwiec et al. (2011, 2012) Kalamkar et al. (2014), Srinivasa et al. (2015) and Oke et al. (2018). In engineering design, modelling (statistical and mathematical models), least squares, non-linear regression, statistical analysis, forward and finite difference methods have been important tools in the determination of unknown parameters. Alfio (2009) stated that mathematical modelling is aim to describe the different aspects of the real world environment, their interactions, and their dynamics through mathematics or mathematical equations and expressions. It constitutes the third pillar of science and engineering, which achieve the fulfilment of the two more traditional disciplines (theoretical analysis and experimentation). It was highlighted that mathematical modeling has a key role in the fields of biomedical, environment and industry. Its potentials contribution in many other areas is becoming more and more evident. Statistical analysis of what arevariously referred to as lifetime, survival time, or failure time data. It is an important topic in many areas, including the biomedical, engineering, and social sciences. The objectives of statistical model and statistical analysis include description or estimation of distributions, comparison of distributions, furthering scientific understanding, process or system improvement, prediction, and decision. In environmental pollution control least squares and non-linear regression methods have been used successfully in determination of BOD parameters, but documentations on utilization of Newton-Raphson method (NRM) for these parameters, its accuracy, validity and good fitness are rare in literature, which calls for immediate solution based on the importance of the BOD parameters and the method. The main objective of this study is to demonstrate the use of NRM for the determination of the parameters and to compare its accuracy, validity and good fitness with other methods. Figure 2 presents a synthetic view of the whole process leading from a problem through modelling to its solution by scientific computations and simulations. The Newton-Raphson method is a widely used numerical method for solving systems of non-linear equations (Oke et al., 2016, 2017). The method is applicable to problems that can be expressed in the form of $F(x) = 0$, where the solution is that the value of x that causes F to become zero. Application of the technique is to a system where there is only one equation with unknown parameters. The derivation of F(x) can be approximated as follows:

$$\frac{dF}{dx} = \frac{F(x + \Delta x) - F(x)}{\Delta x} \quad (8)$$

The solution is obtained by selecting initial value of x, calculating partial derivatives of each F with respect to x and solving the set of linear equations to find a new value of x. The process is repeated until all the calculated F values are sufficiently close to zero. It is well known that BOD kinetics follows first order kinetic and it can be expressed as follows:
\[ Y_T = L_O \left(1 - EXP^{-k}t\right) = L_O \left(1 - 10^{-kt}\right) \] (9)

The linear equation of equation (9) for Newton–Raphson application can be expressed as follows:

\[ \frac{dY_T}{dt} = \frac{Y_{T+1} - Y_{T-1}}{t_{T+1} - t_{T-1}} = kl_O EXPM-k \] (10)

Indicating that \( Y_T = L_O \left(1 - \frac{1}{k} \frac{dY_T}{dt}\right) \) (11)

Equation (11) can be solved in two different ways using matrix and graphical methods. For the graphical method a graph of \( Y_T \) against \( \frac{dY_T}{dt} \) can be used to determine the values of \( k \) and \( L_o \) from the slope and intercept respectively as follows:

\[ Y_T = L_O \left(1 - \frac{1}{k} \frac{dY_T}{dt}\right) = Y = C - MX \] (12)

For the matrix method the above equation (6) was transformed into a set of two equations as follows:

\[ \sum_{n=1}^{N} Y_T = Nt_L = \sum_{n=1}^{N} \frac{dY_T}{dt} \] (13)

\[ \sum_{n=1}^{N} \frac{dY_T}{dt} Y_T = L_O \sum_{n=1}^{N} \left(\frac{dY_T}{dt}\right) + \left(1 - \frac{1}{k} \sum_{n=1}^{N} \frac{dY_T}{dt}\right) \] (14)

The values of \( k \) and \( L_o \) can be determined from equations (12, 13 and 14). Procedures employed in the computations of model constants using Microsoft Excel Solver (MES) are as follows (Oke et al., 2017):

a) Microsoft Excel Solver was added in on the toolbar of Microsoft Excel;

\[ \sum_{i=1}^{N} (Y_T - (L_O - \frac{1}{k} \frac{dY_T}{dt}))^2; \] (15)

b) Target (limit) value of the iteration was set for the software based on square of difference as

c) 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

d) The iteration started through Microsoft Excel Solver (Figure 3).

**Figure 2a: Scientific application of mathematical model at a glance. Source: Alfi, 2009**

More on MES can be found in literature such as Oke et al. (2016; 2017), Barati (2013); Tay et al. (2014) and Hui et al. (2018).

### 2.0 MATERIALS AND METHOD

Wastewater samples were composed from an influent into domestic -institutional waste stabilization ponds of Obafemi Awolowo University, Ile-Ife, Nigeria daily for two weeks. The BOD\(_5\) of the samples were determined daily for the first eight days using Standard Methods as specified in APHA (2012) and van Loosdrecht et al. (2016); using respirometric method (CAMLAB HACH, model number 2173B BOD manufactured by Hach Chemical Company). The procedures and steps were repeated for blanks (to serve as
Figure 2b: Scientific application of mathematical model in medical sciences. (Source: Alfio, 2009)

Figure 3: Procedure for using Microsoft Excel Solver in the computation of adsorption kinetics
controls). The BOD$_c$ were taken directly from the graduated tubes and the readings were multiplied by dilution factor to obtain actual BOD$_c$ (mg/l). Computations of the BOD kinetics' constants (ultimate BOD and rate of BOD concentration removal) were conducted using NRM (graphical and matrix methods using Microsoft Excel Solver), daily difference, Thomas, ratio, two points and least squares methods. Evaluations of the performance of these methods were conducted using Analysis of Variance (ANOVA), errors, statistical reliability, Coefficient of Determination (CD) and Model of Selection Criterion (MSC). The Model of Selection Criterion (MSC) is interpreted as the proportion of expected chloride concentration and observed chloride concentrations variation that can be explained by the obtained chloride concentrations. Higher value of MSC indicates higher accuracy, validity and the good fitness of the method. MSC was computed using equation (18) as follows (Babatola et al., 2008):

$$MSC = \frac{\sum_{i=1}^{n} (Y_{\text{obsi}} - \bar{Y}_{\text{obs}})^2}{n} - \frac{2p}{n} \sum_{i=1}^{n} (Y_{\text{obsi}} - Y_{\text{cali}})^2$$ (16)

where, $Y_{\text{obsi}}$ is the observed concentration; $\bar{Y}_{\text{obs}}$ is the average of observed concentration; $p$ is the total number of fixed parameters to be estimated in the equation; $n$ is the total number of concentration, and $Y_{\text{cali}}$ is the expected concentration.

The total error, which is the sum of the squares of the errors between the obtained values and the predicted values, can be interpreted as a measure of variation in the values predicted unexplained by the values obtained data. The lower the value of total error the higher the accuracy, validity and good fitness of the method. Total error ($Err^2$) can be computed using equation (17):

$$Err^2 = \sum_{i=1}^{n} (Y_{\text{obsi}} - Y_{\text{cali}})^2$$ (17)

The statistical reliability (SR) is interpreted as the proportion of expected data that can be explained by the obtained data. Like, CD and MSC the higher the value of SR, the higher the accuracy, validity, confidence level and the good fitness of the method. SR can be computed using equation (18) as follows (Guttmann et al., 1971):

$$SR = 1 - \frac{\sum_{n=1}^{n} (Y_{\text{obsi}} - Y_{\text{cali}})}{\sum_{n=1}^{n} Y_{\text{obsi}}}$$ (18)

The more appropriate model is the one with the highest calculated SR. Coefficient of determination (CD) can be interpreted as the proportion of expected data variation that can be explained by the obtained data. Higher values of CD indicate higher accuracy, validity and good fitness of the method. CD can be expressed as follows (Babatola et al., 2008):

$$CD = 1 - \frac{\sum_{i=1}^{n} (Y_{\text{obsi}} - \bar{Y}_{\text{cali}})^2}{\sum_{i=1}^{n} (Y_{\text{obsi}} - Y_{\text{cali}})^2}$$ (19)

### 3.0 RESULTS AND DISCUSSION

Figure 4 presents relationship between BOD$_c$ removed and the days. The figure revealed that BOD removed increased with increased number of days. The figure also revealed that these increments were higher at the earlier stage than at the latter stages. Table 1 presents statistical analysis of BOD$_c$. The results of the statistical analysis of BOD using analysis of variance (ANOVA) revealed that there were significant differences between the BOD$_c$ within the samples ($F_{5,35} = 115.76; p = 9.56 \times 10^{21}$) and within the number of days ($F_{7,35} = 192.3982; p = 5.32 \times 10^{-26}$) at 99% confidence level. Table 2 shows ultimate BOD (UBOD) for all the methods and samples. The ultimate BOD ranges from 822 mg/l to 1691 mg/l originated from ratio and Thomas methods respectively. These UBOD were similar to the ultimate BOD documented in literature for domestic-institutional wastewater. Metcalf and
Eddy (1991) classify wastewaters with this range of UBOD as strong domestic wastewaters. Table 3 reveals statistical analysis (2 ways ANOVA) of the UBOD. The table revealed that there were significant differences between UBOD from the methods ($F_{3.45} = 8.957; p = 1.39 \times 10^{-3}$) and various UBOD from samples ($F_{4.45} = 16.712; p = 2.61 \times 10^{-6}$) at 99% confidence level. These BOD$_c$ and UBOD revealed that BOD$_c$ and UBOD are function of the sample (source of wastewaters) and the method used in the determination of the UBOD. It indicated that the BOD$_c$ and UBOD vary with the method of determinations used, samples and period.

![Figure 4: Relationship between BOD$_c$ removed and the days](image)

<table>
<thead>
<tr>
<th>Table 1: Statistical Analysis of BOD</th>
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<tr>
<td>Source of Variation</td>
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<tr>
<td>Days</td>
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<td>Samples</td>
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<tr>
<td>Total</td>
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<tr>
<th>Table 2: The values of ultimate BOD and rate of reaction</th>
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<tr>
<td>Methods</td>
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<tr>
<td>Sample 1</td>
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<td>Sample 2</td>
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<td>Sample 3</td>
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<td>Sample 4</td>
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<td>Sample 5</td>
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<td>Sample 6</td>
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<tr>
<td>Non-linear regression</td>
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<td>Least Square</td>
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<tr>
<td>Thomas</td>
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<td>Pajimoto</td>
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<td>Ratio</td>
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<td>Logarithms difference</td>
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<tr>
<td>Two Points</td>
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<tr>
<td>Daily difference</td>
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<td>Newton- Raphson</td>
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<tr>
<td>Matrix</td>
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<tr>
<td>Graphical</td>
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<table>
<thead>
<tr>
<th>Table 3: statistical analysis of UBOD</th>
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<tr>
<td>Source of Variation</td>
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<tr>
<td>Methods</td>
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<tr>
<td>Samples</td>
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<tr>
<td>Error</td>
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Table 4: Statistical Analysis of kBODr

<table>
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<th>Source of Variation</th>
<th>Sum of Squares</th>
<th>Degree of freedom</th>
<th>Mean Sum of Square</th>
<th>F- Value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methods</td>
<td>0.221368</td>
<td>9</td>
<td>0.024596</td>
<td>7.898823</td>
<td>7.02 x 10^-67</td>
</tr>
<tr>
<td>Samples</td>
<td>0.160757</td>
<td>5</td>
<td>0.032151</td>
<td>10.32498</td>
<td>1.23 x 10^-66</td>
</tr>
<tr>
<td>Error</td>
<td>0.140127</td>
<td>45</td>
<td>0.003114</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>0.522252</td>
<td>59</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2 presents rate of carbonaceous BOD removal (kBODr). The table revealed that the minimum value was -0.1350 /d and -0.621 /d as the maximum originated from Ratio and daily difference methods respectively. Table 4 reveals statistical analysis (2 ways ANOVA) of the kBODr. The table revealed that there were significant differences between kBODr from the methods (F<sub>.05</sub> = 7.90; p = 7.02 x 10^-5) and various kBODr from samples (F<sub>.05</sub> = 10.32; p = 1.23 x 10^-6) at 99% confidence level. These kBODr, BOD<sub>c</sub> and UBOD revealed that kBODr, BOD<sub>c</sub> and UBOD are function of the sample (source of wastewaters) and the method used in the determination of the UBOD. It indicated that the kBODr, BOD<sub>c</sub> and UBOD vary with the method of determinations used, samples and period.

**Statistical Analysis of the Methods:** Tables 5 and 6 present statistical evaluations of the methods. The total error calculated for these methods ranged from 8.5 to 1516 (Table 5) with the lowest error came from non-linear regression method followed by logarithm difference and Newton Raphson methods. The largest error originated from ratio method. The CD computed for the methods ranged from 0.603 to 1.000 with the highest CD calculated came from non-linear regression and logarithm difference methods. The lowest CDs calculated are for ratio and Fujimoto's methods. MSC computed for the methods ranged from 0.24 to 9.88 (Table 6) with the lowest MSC originated from ratio and Fujimoto methods. The largest MSC calculated came from non-linear regression, Newton Raphson and logarithm difference methods in all cases. SR computed for all these methods ranged from 0.513 to 0.999 (Table 6) out of 1.000 with the lowest SR calculated is coming from ratio and Fujimoto methods. The largest SR computed is coming from non-linear regression and logarithm difference methods.

Tables 7, 8, 9 and 10 show statistical analysis of total errors, CD MSC and SR, respectively. Table 7 shows statistical analysis of total errors. Statistical analysis of the computed total error shows that there was significant difference between the methods (F<sub>.05</sub> = 63.52; p = 1.32 x 10^-25) and within the samples F<sub>.05</sub> = 4.17; p = 3.40 x 10^-3) at 99% confidence level. Table 8 shows statistical analysis of CDs. Statistical analysis of the computed CD shows that there was significant difference between the methods (F<sub>.05</sub> = 113.89; p = 6.10 x 10^-28) at 99% confidence level and no significant difference within the samples F<sub>.05</sub> = 2.25; p = 6.6 x 10^-4) at 90% confidence level. Table 9 shows statistical analysis of MSCs. Statistical analysis of the computed MSC shows that there was significant difference between the methods (F<sub>.05</sub> = 77.04; p = 2.4 x 10^-26) and there was no significant difference within the samples F<sub>.05</sub> = 2.21; p = 7.01 x 10^-3) at 99% confidence level. Table 10 shows statistical analysis of SRs. Statistical analysis of the computed SR shows that there was significant...
difference between the methods ($F_{0.45} = 370.43; p = 3.9 \times 10^{-39}$) at 99% confidence level and no significant difference within the samples $F_{0.45} = 1.58; p = 1.86 \times 10^{-7}$) at 99% confidence level. All the results indicated that there were significant differences between the performance and accuracies of these methods.

**Summary of the Analysis and Evaluations:**

ANOVA methods are in effect a generalisation of two samples procedures. ANOVAs are essentially attempt to separate mathematically the total variation within the experimental measurements into sources corresponding to the elements controlled within the experiment the factors studied and the elements not controlled the unexplained variation or experimental error from this the variation due to controlled factors, which can be compared to that of the unexplained variation and large ratios (F-ratio) signifying a significant explainable effect. ANOVAs provide statistical test element of experimental design. Detail explanation of ANOVA can be found in literature such as Guttman *et al.*, (1978) The ANOVA for the two approaches for NRM was carried out (Table 11).

<table>
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<tr>
<th>Methods</th>
<th>Total error</th>
<th>CD</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Sample 1</td>
<td>Sample 2</td>
</tr>
<tr>
<td>Non-linear regression</td>
<td>40.9</td>
<td>50.9</td>
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<tr>
<td>Least Square</td>
<td>121.76</td>
<td>80.23</td>
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<tr>
<td>Thomas</td>
<td>114.5</td>
<td>88.2</td>
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<tr>
<td>Fujimoto</td>
<td>1516</td>
<td>1225</td>
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<tr>
<td>Ratio</td>
<td>1420</td>
<td>1145</td>
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<td>Logarithms difference</td>
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<td>Daily difference</td>
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<table>
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<th>MSC</th>
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<td>Newton-Raphson</td>
<td>6.02</td>
<td>6.10</td>
</tr>
<tr>
<td>Graphical</td>
<td>5.92</td>
<td>6.31</td>
</tr>
</tbody>
</table>
### Table 7: Statistical Analysis of Total Error

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>Sum of Squares</th>
<th>Degree of Freedom</th>
<th>Mean Sum of Square</th>
<th>F- Value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methods</td>
<td>9130810</td>
<td>9</td>
<td>1014534</td>
<td>63.51599</td>
<td>1.32 x 10^{-22}</td>
</tr>
<tr>
<td>Samples</td>
<td>332669.1</td>
<td>5</td>
<td>66533.81</td>
<td>4.165419</td>
<td>0.003401</td>
</tr>
<tr>
<td>Error</td>
<td>718780.3</td>
<td>45</td>
<td>15972.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>10182259</td>
<td>59</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 8: Statistical Analysis of CD

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>Sum of Squares</th>
<th>Degree of Freedom</th>
<th>Mean Sum of Square</th>
<th>F- Value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methods</td>
<td>0.787504</td>
<td>9</td>
<td>0.0875</td>
<td>113.8766</td>
<td>6.1 x 10^{-28}</td>
</tr>
<tr>
<td>Samples</td>
<td>0.008627</td>
<td>5</td>
<td>0.001725</td>
<td>2.245526</td>
<td>0.065972</td>
</tr>
<tr>
<td>Error</td>
<td>0.034577</td>
<td>45</td>
<td>0.000768</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>0.830709</td>
<td>59</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 9: Statistical Analysis of MSC

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>Sum of Squares</th>
<th>Degree of Freedom</th>
<th>Mean Sum of Square</th>
<th>F- Value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methods</td>
<td>370.649</td>
<td>9</td>
<td>41.18323</td>
<td>77.03952</td>
<td>2.4 x 10^{-24}</td>
</tr>
<tr>
<td>Samples</td>
<td>5.897993</td>
<td>5</td>
<td>1.179599</td>
<td>2.20662</td>
<td>0.070123</td>
</tr>
<tr>
<td>Error</td>
<td>24.05577</td>
<td>45</td>
<td>0.534573</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>400.6028</td>
<td>59</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 10: Statistical Analysis of Reliability

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>Sum of Squares</th>
<th>Degree of Freedom</th>
<th>Mean Sum of Square</th>
<th>F- Value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methods</td>
<td>1.509178</td>
<td>9</td>
<td>0.167686</td>
<td>370.4316</td>
<td>3.9 x 10^{-39}</td>
</tr>
<tr>
<td>Samples</td>
<td>0.003571</td>
<td>5</td>
<td>0.000714</td>
<td>1.577779</td>
<td>0.185716</td>
</tr>
<tr>
<td>Error</td>
<td>0.020371</td>
<td>45</td>
<td>0.000453</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>1.533119</td>
<td>59</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 11: Statistical Analysis of NRM (Graphical and Matrix)

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>Sum of Squares</th>
<th>Degree of Freedom</th>
<th>Mean Sum of Square</th>
<th>F- Value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methods</td>
<td>3.836918</td>
<td>1</td>
<td>3.836918</td>
<td>0.466001</td>
<td>0.501651</td>
</tr>
<tr>
<td>Analysis</td>
<td>34284.45</td>
<td>23</td>
<td>1490.628</td>
<td>181.0397</td>
<td>6.67 x 10^{-21}</td>
</tr>
<tr>
<td>Error</td>
<td>189.3753</td>
<td>23</td>
<td>8.233711</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>34477.67</td>
<td>47</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
This result indicates that there is no significant difference between the two approaches of NRM used. The table revealed that within the two solutions of NRM there was no significant ($F_{1,23} = 0.466$, $p = 0.502$) difference in terms of their accuracies and performances at 99% confidence level. The results of statistical assessment (evaluation) are presented in Tables 5 and 6. It is clear that using non-linear regression method (NLR), Newton Raphson and logarithms difference (LD) method resulted (in all cases) in the smallest error, the highest values of CD, SR and MSC. The computed statistical evaluation (total error, CD, SR and MSC) indicate that non-linear regression, Newton Raphson (NRM), or logarithms difference methods should be the first choice out of the selected methods when considering analysis of BOD results for UBOD and $k$BODr determination at more than 97.0% (average SR= 0.997, 0.972 and 0.998 for NLR, NRM and LD respectively) reliability (confidence level). These results were similar to observation made on non-linear regression (the method is the best approach to polynomial equations such as BOD removal, Gullemo et al., 1999). The only difference between logarithms difference, Newton Raphson methods and non-linear regression method is that the methods (LD and NRM) can easily be implemented in an electronic spreadsheet, Microsoft excels and Microsoft words graphically and otherwise.

The least squares method is the next to NLR and LD in ranking in all cases. Although, the method can be easily implemented in an electronic spreadsheet, Microsoft excels and most plotting packages have it built in too. The drawback is that it gives larger errors than non-linear regression, Newton Raphson and logarithms difference methods, lower CD and MSC. These drawbacks are due to the discrete of fitting a curve into a linear equation at each of the data points. The daily difference method (which is next in term of validity and accuracy, is also easy to be implemented) originated from mathematical function of first derivative of BOD equation. The results of total error, CD and MSC show that the mathematical function is always true for the kinetic, but the method had average statistical reliability values of 0.974 out of 1.00. This result indicates that for statistical reliability of higher than 0.974 the method cannot be used or the method is not reliable beyond 97.4% accuracy.

Thomas method (which is next in term of validity and accuracy, is easy to be implemented) originated from the similarity in shapes of an arbitrary mathematical function with that of the BOD curve. The results of total error, CD and MSC show that the mathematical function is always true for BOD curve, but had average statistic reliability values of 0.951 out of 1.00. This result indicates that for statistical reliability of higher values than 0.965 the method cannot be used. Two points methods has the next higher calculated CD and MSC. Although, the method do not have any mathematical expression but can be said to have given room for error reduction by selecting two days of higher distance apart. The Fujimoto and ratio methods have the lowest ranks, the largest total error, and the lowest CD, statistical reliability and MSC. Although, these two methods can be implemented manually easily on an electronic spreadsheet, Microsoft excels and most plotting packages have them built in too. Their drawback is that they give larger errors due to the discrete estimation of the slope and ratios, which are made at each of the data points.

**CONCLUSION**

Based on the results of statistical evaluation it can be concluded that:
i. Newton-Raphson can be used for BOD kinetics parameters determination,

ii. the methods (Newton-Raphson) are statistically and mathematically valuable,

iii. Non-linear regression, logarithms difference, Newton-Raphson, least squares or Thomas methods should be the first method of choice when making BOD parameters estimation. Although, it can be argued that Newton-Raphson and non-linear methods are more difficult to implement, the extended use of computers and the existence of computer packages or routines for non-linear and Newton-Raphson parameter estimation would made its implementation much simpler.

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