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Simplistic approach for evaluating the BOD rate constants

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Biochemical oxygen demand (BOD) is the most important biological parameter of wastewater for designing the biological treatment system of the same. Traditionally, BOD_5 at 20°C (or BOD_3 at 27°C) is determined, and ultimate BOD (L_0) is calculated from the classical equation of BOD exertion using BOD exertion rate (k). Therefore, the value of k is determined from a set of intermediate BOD values measured within 5 or 3 days. The present methods of determination of L_0 and k need at least three BOD data for suitable linearization of BOD exertion equation. It requires a long period for obtaining three BOD data, which can be reduced to two BOD data in the proposed method. The unique feature of this simplistic method is the use of two BOD data only at the time periods, in multiple of 2. The method has been compared with the conventional methods using several BOD data sets, which showed satisfactory results.

Keywords: BOD rate constants, BOD exertion rate, ultimate BOD, simplistic method, two BOD data, comparative study.

Introduction

Evaluation of the ultimate BOD (L_0) is extremely required in designing the biological system for wastewater treatment. Determination of the ultimate BOD practically in the laboratory is a prolong process, therefore, 5 day BOD at 20°C or 3 day BOD at 27°C is determined and from that BOD value the ultimate BOD can be determined, if value of BOD exertion rate, k is known. The 'k' can be determined by various analytical methods like Least Square method, Thomas graphical method, Fujimoto method, Bagchi and Chaudhuri method, etc. In all of these methods the BOD exertion equation based on first order kinetics is used[3,4,6,8,10] which is considered the most accepted model[1].

$$BOD_t = L_o\,(1 - e^{-kt}) \qquad (1)$$

BOD_t = Amount of organic matter in terms of oxygen consumed in time t (mg/L)

t = Time interval between start of the test and when the reading is taken (day)

L_0 = Ultimate BOD (mg/L)

k = BOD reaction rate constant (day^{-1})

In order to determine the BOD rate constant 'k' a series of BOD values with an interval of usually one day is measured with initial and final BOD_5 and these results are used to estimate the BOD rate constant using the methods as stated above. All these methods of determination of L_0 and k need at least three BOD data for suitable linearization of BOD exertion equation. It demands for a long period for having three BOD data, which can be reduced to two BOD data in the proposed method. The important feature of this simplistic method is the use of two BOD data only corresponding to the time periods, in multiple of 2. Analytical derivation of the method is associated with a simple quadratic equation, which can be solved using two BOD data. The proposed method has been compared with the current methods like method of Least Square, Thomas method, Fujimoto method and Bagchi and Chaudhuri method using available five BOD data sets. It reveals that the proposed method is satisfactory even in case of two BOD data are available for each set. Moreover, the proposed method is easy to implement with very little calculations and without any requirement of plotting a graph.

Material and methods

Analytical methods for determination of BOD rate constants:

Thomas graphical method:

The Thomas method is based on functional similarity. This method utilizes the similarity of the series expansion of the following functions[5,11,12]

$$F_1 = (1 - e^{-kt}) \quad (2)$$

$$F_2 = (kt)[1 + (1/6)kt]^{-3} \quad (3)$$

The expansion of the functions yields the following expressions,

$$F_1 = (kt)\{1 - (1/2)kt + (1/6)(kt)^2 - (1/24)(kt)^3 + ...\} \quad (4)$$

$$F_2 = (kt)\{1 - (1/2)kt + (1/6)(kt)^2 - (1/21.6)(kt)^3 + ...\} \quad (5)$$

The first three terms of the above expressions are identical and the fourth term deviates a little. Correlating the BOD equation, eq. (1) with eqs. (4) and (5) we can have the following equation,

$$BOD_t = L_0\,(kt)\,[1 + (1/6)kt]^{-3} \quad (6)$$

Rearranging the terms and taking cube root of the both sides in eq. (6) we get,

$$\left(\frac{t}{BOD_t}\right)^{1/3} = \frac{1}{(kL_0)^{(1/3)}} + \frac{(k)^{2/3}}{6(L_0)^{(1/3)}}(t) \quad (7)$$

where, L_0 = ultimate BOD and k = BOD reaction rate constant,

From eq. (7) $\left(\frac{t}{BOD_t}\right)^{1/3}$ vs t graph can be plotted and a best fitted straight line can be drawn with an intercept of A and slope of B. The slope and the intercept is given by the following expression

$$B = \frac{(k)^{2/3}}{6(L_0)^{(1/3)}} \quad (8)$$

$$A = (kL_0)^{-(1/3)} \quad (9)$$

From eqs. (8) and (9) the values of ultimate BOD and BOD reaction constant can be obtained as,

$$k = 6\frac{B}{A} \quad (10)$$

$$L_0 = \frac{1}{6(A)^2(B)} \quad (11)$$

Method of Least Square:

This method is based on minimizing the error between the best fitted curve and the series of data points collected after laboratory measurement of BOD on the same sample (Metcalf and Eddy Inc., 2004).The change of BOD with time for each time interval can be expressed through the following equation,

$$\frac{dy}{dt} = k\,(L_0 - y) \quad (12)$$

In eq. (12) the values of k and L_0 need to be estimated. If $\frac{dy}{dt}$ represents the slope of the best fitted curve of all the data points for a given k and L_0, then because of some experimental error the left side and right side values of the eq. (12) will differ by an amount say, R.

$$\text{So, } R = k\,(L_0 - y) - \frac{dy}{dt}$$

$$\text{or, } R = kL_0 - ky - y' \quad (13)$$

Substituting a for kL_0 and –b for k, eq. (13) can be rewritten as,

$$R = a + by - y' \quad (14)$$

Now, for R to be minimum, the following conditions must be satisfied

$$\frac{\partial}{\partial a}\Sigma R^2 = \Sigma 2R\frac{\partial R}{\partial a} = 0 \quad (15a)$$

$$\text{and, } \frac{\partial}{\partial b}\Sigma R^2 = \Sigma 2R\frac{\partial R}{\partial b} = 0 \quad (15b)$$

Now, replacing $R = a + by - y'$ in eqs. (15a) and (15b) following expressions can be derived,

$$na + b\Sigma y = \Sigma y' \quad (16a)$$

$$a\Sigma y + b\Sigma y^2 = \Sigma yy' \quad (16b)$$

where, n = number of data points

Δt = Time interval (day)

$$\text{and } y' = \frac{(y_{n+1} - y_{n-1})}{2\Delta t}$$

Solving eqs. (16a) and (16b), values of k and L_0 can be determined as

$k = -b$ and $L_0 = -(a/b)$

Fujimoto method:

Fujimoto developed a graphical solution for determining the ultimate BOD (L_0) and the BOD reaction rate constant (k). In this method the expression of BOD exertion after (t+h) day can be written as,

$$y_{t+h} = L_0 (1 - e^{-kh}) + e^{-kh} . y_t \quad (17)$$

where, y_t = BOD exerted in time t and y_{t+h} = BOD exerted in time (t+h).

A graph can be plotted with y_{t+h} as ordinate and y_t as abscissa, which has a slope of e^{-kh}. If the BOD data are collected at a constant time interval h, the value of L_0 is determined in this method from the intersection of two straight lines given by eq. (17) and $y_t = y_{t+h}$. Then k value can be determined from the slope of this graph using the value of h.

Bagchi-Chaudhuri method:

This method is a modification over Fujimoto method. Fujimoto is method is applicable when the BOD data are collected with a constant time interval, h. In this method the aforesaid limitation is omitted by modifying the eq. (17) as follows.

Subtracting y_t from both sides of the eq. (17)

$$y_{t+h} = L_0 (1 - e^{-kh}) - y_t (1 - e^{-kh})$$

$$\text{Hence, } \frac{y_{t+h} - y_t}{L_0 (1 - e^{-kh})} + \frac{y_t}{L_0} = 1 \quad (18)$$

The eq. (18) can be represented in graphical form with $(y_{t+h} - y_t)$ as ordinate and y_t as abscissa.

Therefore, L_0 = Intercept in x-axis = m

$L_0 (1 - e^{-kh})$ = Intercept in y-axis = n

Using the value of L_0, 'k' can be determined as follows.

$$k = \frac{1}{h} \ln \frac{L_0}{L_0 - n} \quad (19)$$

Proposed method:

In this method only two data are sufficient to get the value of BOD reaction rate constant (k) and ultimate BOD (L_0), provided that the second data must be taken at twice the time interval of collection of first data from start of the test. The BOD exertion as per eq. (1) can be expressed for two such time interval T and 2T as follows.

$$y_1 = L_0 (1 - e^{-Tk}) \quad (20a)$$

$$y_2 = L_0 (1 - e^{-2Tk}) \quad (20b)$$

where, y_1 and y_2 are known BOD values, T is the time interval of first data collection.

$$\text{Therefore, } \frac{y_1}{y_2} = \frac{(1 - e^{-Tk})}{(1 - e^{-2Tk})} \quad (21)$$

$$\text{Substituting } e^{-Tk} \text{ by x in eq. (21), } \frac{y_1}{y_2} = \frac{1-x}{1-x^2}$$

$$\text{or, } \frac{y_1}{y_2}(1-x^2) = 1-x$$

$$\text{or, } \frac{y_1}{y_2} x^2 - x + \left(1 - \frac{y_1}{y_2}\right) = 0 \quad (22)$$

Solving eq. (22) the value of x can be determined as p (say).

$$\text{Therefore, } k = -\frac{\ln p}{T} \quad (23)$$

If the value of k is known, the value of L_0 can be calculated from either eq. (20a) or (20b).

Results and discussion

Illustrative examples of aforesaid methods on the same data set.

The experimental values of five BOD data sets are given in Tables 1–5 below. The aforesaid methods are used on all the data sets to find BOD rate constant, k and ultimate BOD, L_0.

Table 1. Experimental values of BOD for an untreated wastewater[5]

Day	0	1	2	4	6	8
BOD (mg/L)	0	32	57	84	106	111

Table 2. Experimental values of BOD[3]

Day	0	1	2	3	4	5
BOD (mg/L)	0	60	70	90	100	120

Note: This data is of raw sewage from a brewery industry.

Table 3. BOD data used for establishing novel method[2]

Day	0	1	2	3	4	5	6	7	10
BOD (mg/L)	0	20.6	37	50	60	68	75	80	90

Note: The original data was given by Sawyer *et al.*, (1960)[9].

Table 4. Experimental values of BOD[7]

Day	0	1	2	3	4	5	6	7
BOD (mg/L)	0	82	112	153	163	176	192	200

Note: This data is of a raw sewage from a military installation.

Table 5. Experimental values of BOD[6]

Day	0	2	4	6	8	10
BOD (mg/L)	0	11	18	22	24	26

Note: This data is of a stream receiving some treated effluent.

Solution by Thomas method:

At first the values of $(t/BOD_t)^{1/3}$ are calculated in Table 6 using the BOD data set as given in Table 1.

Table 6. Computation of $(t/BOD_t)^{1/3}$ in Thomas method

Day	0	1	2	4	6	8
$(t/BOD_t)^{1/3}$	–	0.315	0.327	0.362	0.384	0.416

The plot of $(t/BOD_t)^{1/3}$ vs t is shown Fig. 1, wherefrom the intercept (A) and slope (B) can be estimated as

$A = 0.3\ [\text{day}/(\text{mg/L})]^{1/3}$ and $B = 0.0144\ [(\text{day})^{-2/3}/(\text{mg/L})^{1/3}]$

From eqs. (10) and (11) we have

$$k = 6\,\frac{B}{A} = 0.288\ \text{day}^{-1}$$

$$\text{and } L_0 = \frac{1}{6(A)^2(B)} = 128.6\ \text{mg/L}$$

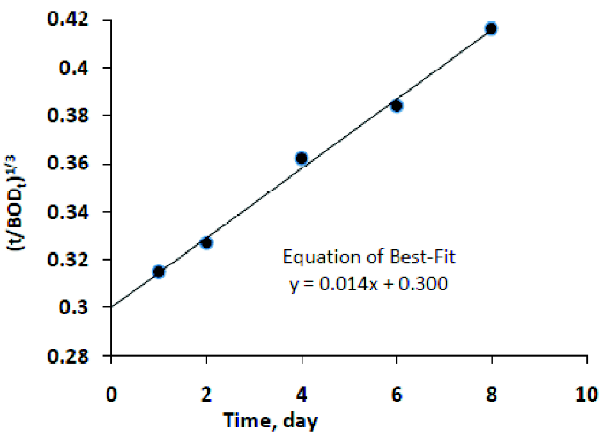

Fig. 1. Determination of L_0 and k by Thomas method.

Solution with method of Least Square:

In this method (Metcalf and Eddy Inc., 2004), the values of y, y^2, y' and yy' are computed using the BOD data set as given in Table 1 and shown in Table 7.

Table 7. Computation of y, y^2, y' and yy' in method of least square

Time (day)	y	y^2	y'	yy'
0	0	0	–	–
1	32	1024	28.5	912
2	57	3249	17.33	987.8
4	84	7056	12.25	1029
6	106	11236	6.75	715.5
8	111[a]	12321[a]	–	–
	Σy = 279	Σy^2 = 22565	$\Sigma y'$ = 64.83	$\Sigma yy'$ =3644.3

[a]Value not taken in summation.

Substituting the values in eqs. (16a) and (16b),

$$4a + 279b - 64.83 = 0 \quad (24a)$$

$$279a + 22565b - 3644.3 = 0 \quad (24b)$$

Solving eqs. (24a) and (24b) the values of a and b are calculated as,

$a = 35.877\ (\text{mg/L})(\text{day}^{-1})$ and $b = -0.282\ \text{day}^{-1}$

Now, $k = -b = 0.282\ \text{day}^{-1}$

Ultimate BOD, $L_0 = -(a/b) = -(35.877/-0.282) = 127.22$ mg/L.

Solving with Fujimoto method:

There are 4 (four) BOD data in the set given in Table 1, which were measured at 2 days time interval. Accordingly, the equal time interval is taken as 2 days and the values of y_{t+h} and y_t are set out as shown in Table 8. Accordingly, y_{t+h} data can be plotted with respect to y_t as shown in Fig. 2.

Table 8. Values of y_{t+h} and y_t in Fujimoto method

y_t	0	57	84	106
y_{t+h}	57	84	106	111

The value of Ultimate BOD (L_0) can be obtained from the intercept of two lines (Metcalf and Eddy Inc., 2004) as

L_0 = 121 mg/L and e^{-kh} = Slope of the Mean Line = 0.525

Therefore, $k = -\ln(0.525)/2 = 0.322\ \text{day}^{-1}$

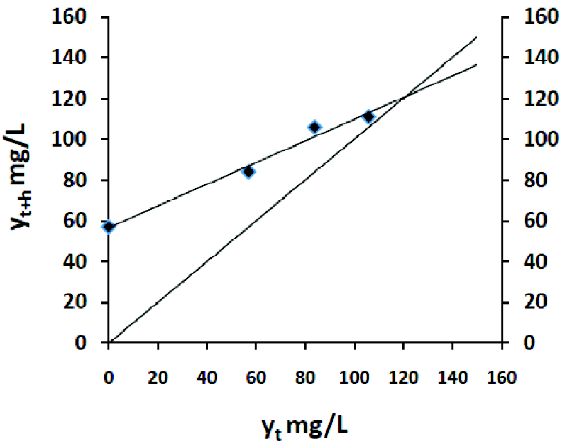

Fig. 2. Determination of L_0 and k by Fujimoto method.

Solution with Bagchi-Chaudhuri method:

There are 4 (four) BOD data in the set given in Table 1, which were measured at 2 days time interval. Accordingly, the equal time interval is taken as 2 days and the values of y_t and $(y_{t+h} - y_t)$ are set out as shown in Table 9. Accordingly, $(y_{t+h} - y_t)$ data can be plotted with respect to y_t as shown in Fig. 3.

Table 9. Values of $(y_{t+h} - y_t)$ and y_t in Bagchi-Chaudhuri method

y_t	0	57	84	106
$(y_{t+h} - y_t)$	57	27	22	5

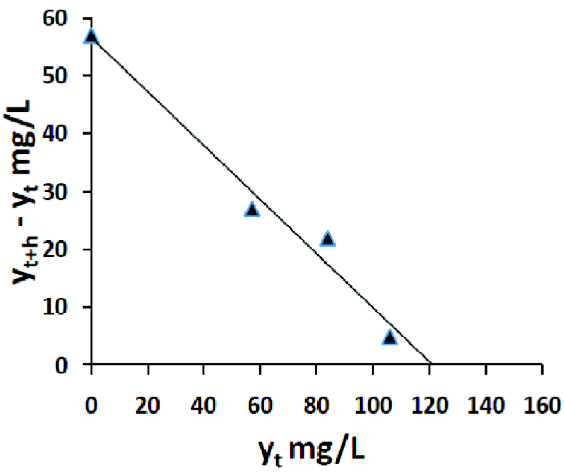

Fig. 3. Determination of L_0 and k by Bagchi-Chaudhuri method.

The value of Ultimate BOD (L_0) can be obtained from the X-intercept of the Mean Line as,

L_0 = 121 mg/L and $L_0(1 - e^{-kh})$ = Y-Intercept of the Mean Line = 57 mg/L.

Therefore, k = –ln (0.529)/2 = 0.318 day^{-1}.

Solution by the proposed method:

In the proposed method BOD data in the set given in Table 1 are sorted in such a way that the time of successive measurement is twice the time of predeceasing observation as shown in Table 10.

Table 10. Sorted BOD data set used in the proposed method

Day	1	2	4	8
BOD (mg/L)	32	57	84	111

Substituting the values of y_1 and y_2 in the eq. (22) for different values of n, following equations can be written,

$$\frac{32}{57}x_1^2 - x_1 + \left(1 - \frac{32}{57}\right) = 0 \quad \text{(for T = 1 day)} \tag{25a}$$

$$\frac{57}{84}x_2^2 - x_2 + \left(1 - \frac{57}{84}\right) = 0 \quad \text{(for T = 2 days)} \tag{25b}$$

$$\frac{84}{111}x_3^2 - x_3 + \left(1 - \frac{84}{111}\right) = 0 \quad \text{(for T = 4 days)} \tag{25c}$$

Eqs. (25a), (25b) and (25c) are independently solved to determine the values of x_1, x_2 and x_3 as 0.781, 0.473 and 0.321 respectively.

Now, $x_1 = e^{-k}$ = 0.781 i.e. k = 0.247 day^{-1}

$x_2 = e^{-2k}$ = 0.473 i.e. k = 0.374 day^{-1}

$x_3 = e^{-4k}$ = 0.321 i.e. k = 0.284 day^{-1}

Hence, the mean value of k = 0.302 day^{-1}.

The value of L_0 can be calculated for four BOD data (as given in Table 6) as 122.8, 125.7, 119.8 and 121.9 mg/L, the mean of which is 122.55 mg/L. The L_0 can also be calculated using the k value obtained for T = 2 which involves data of 2-day and 4-day BOD. Thus L_0 is calculated to be 108.4 mg/L.

All the above stated methods have been performed on the other four data sets also, furnished in Tables 2–5 to find out the k and L_0 values. The results obtained in respect of k and L_0 for all the data sets are shown in Table 11a and Table 11b respectively.

Table 11a. Values of BOD rate constant (k) determined by various methods

Data Set No.	Name of the method					
	Thomas method	Method of least square	Fujimoto method	Bagchi-Chaudhuri method	Proposed method	Proposed method (2-4 day value)
1	0.288	0.282	0.322	0.318	0.302	0.374
2	0.532	0.400	0.605	0.610	1.108	0.424
3	0.242	0.240	0.231	0.241	0.231	0.238
4	0.410	0.406	0.465	0.467	0.618	0.393
5	0.230	0.271	0.260	0.249	0.250	0.226

Table 11b. Comparison of Ultimate BOD (L_0) determined by various methods

Data Set No.	Name of the method					
	Thomas method	Method of least square	Fujimoto method	Bagchi-Chaudhuri method	Proposed method	Proposed method (2-4 day value)
1	128.6	127.2	121.0	121.0	122.5	108.4
2	123.2	130.0	116.0	116.0	89.8	122.5
3	99.3	98.0	100.0	100.0	99.9	97.8
4	210.5	209.7	200.0	201.0	178.4	205.6
5	29.7	27.7	27.5	28.0	28.4	27.0

Comparison of BOD rate constants estimated by various methods:

Thomas graphical method, Fujimoto method and Bagchi-Chaudhuri method are graphical methods, which require many data points to obtain a realistic and dependable value of BOD reaction rate constant and ultimate BOD. Moreover, there exists approximation in the process of framing out the eq. (7) in Thomas method and also while drawing the best fit curve on graph sheet, eye estimation is often used in these methods. On the other hand, the analytical process of method of least square does not require any plotting of graph but it is cumbersome as it takes much calculation even before framing the equations. It also necessitates solution of two linear equations in order to determine k and L_0. There is no recent study, on simplistic approach for determination of L_0 and k, to be compared to the proposed method.

In the proposed method only two BOD data are enough to estimate the ultimate BOD as well as BOD rate constants of any wastewater sample. Apart from that, there is no need to plot a graph and thereafter to draw the best-fit line, for linearization of the process. Only two BOD data measured at the time intervals, twice the first one are required in this method. As there are more than two data available for the above BOD data sets, complying the requirement for this method also, arithmetic mean has been taken to get values of L_0 and k. The values of BOD rate constants, k and L_0 as shown in Table 11a and Table 11b are also presented as bar diagram in Fig. 4a and Fig. 4b respectively.

Table 11a and Table 11b reveal that the 'k' and 'L_0' values obtained from various conventional methods do not deviate considerably from each other except mean values in case of the proposed method. However, the 'k' values from the sec-

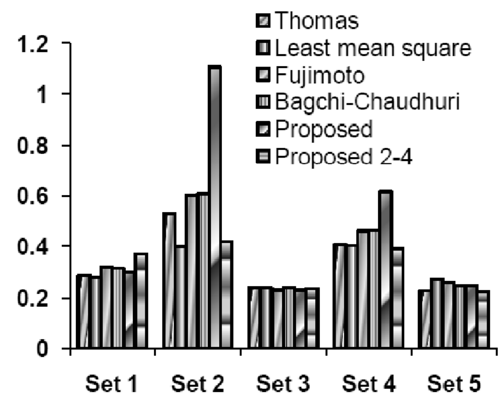

Fig. 4a. Comparison of BOD rate constant k determined by various methods.

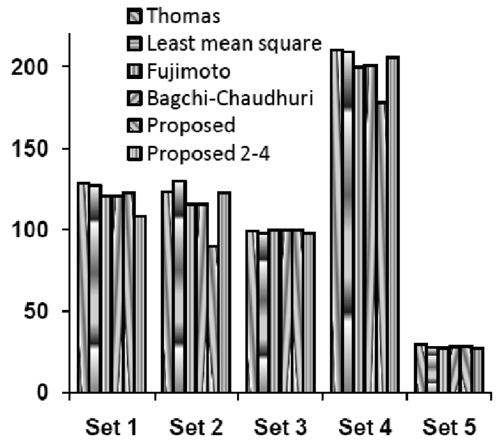

Fig. 4b. Comparison of ultimate BOD L_0 determined by various methods.

ond set of data shows very much unrealistic value when the mean value is taken in the proposed method. Furthermore, the 'k' values for the other data sets also did not exhibit comparable result, when calculated with 1 and 2 day BOD values. This is also to observe that, 2 and 4 day BOD values resulted in more accurate values for 'k' as well as 'L_0' in most cases under the proposed method. Thus it can be suggested to use 2-4 day BOD values to determine the 'k' and 'L_0' values, when only two BOD data to be taken in the proposed method.

Conclusions

Out of various methods available for determination of BOD rate constants – L_0 and k, Thomas and Least Square method involve approximation to some extent. Amongst these, the method of least square requires lengthy and cumbersome analytical calculations. The rest two methods, viz. Fujimoto and Bagchi and Chaudhuri methods are associated with graphical plots, necessitating BOD data at regular time interval. The accuracy of such methods is obviously higher for large numbers of data only. In contrary to that the proposed method needs only two BOD data to determine BOD rate constants using a simplistic procedure. The second data must be taken after twice the time interval of the first one from initiation of the test, which can conveniently be adjusted. This can be regarded as a fast method of determination of BOD rate constants because it involves solution of a quadratic equation only for each two BOD data. It can also be concluded that the 2 and 4 day BOD data yield more accurate 'k' and 'L_0' values, in case of the proposed method.

References

1. B. Y. Ammary and L. A. Al-Samrraie, *Int. J. Environment and Waste Management*, 2014, **13(4)**, 362.
2. D. Bagchi and N. Chaudhuri, *Water Pollution Control Federation*, 1970, R136.
3. F. Bassa and S. Chetty, 'Determination of biodegradable COD fraction of industrial effluents by measurements of BOD and COD', Proceedings of the Biennial Conference of the water Institute of Southern Africa (WISA), 2002, pp.135-143.
4. G. Cutters, L. Manfredi, C. E. Del Valle and J. F. González, *Water SA*, 1999, **25(3)**, 377.
5. D. Cornwell, "Introduction to Environmental Engineering", McGraw-Hill, Int. 1998, ISBN 10: 0071152342 / ISBN 13: 9780071152341.
6. L. Metcalf and H. P. Eddy Inc., "Wastewater Engineering Treatment Disposal and Reuse", Mc-Graw Hill, New York, 2004, 3rd ed.
7. E. W. Moore, H. A. Thomas, W. B. Snow and C. C. Ruchhoft, "Simplified method for analysis of BOD data [with discussion]", Sewage and Industrial Wastes, 1950, 1343-1355.
8. R. S. Ramalho, |Introduction to Wastewater Treatment", Academic Press, New York, 1977.
9. C. N. Sawyer, "Chemistry for Sanitary Engineers", McGraw-Hill Book Company, Inc., New York, 1960.
10. E. W. Steel and T. J. McGhee, "Water Supply and Sewerage", McGraw-Hill Company, New York, 1991.
11. H. A. Thomas, 'Graphical determination of BOD curve constants', Water Sewage Works, 1950, March, Vol. 97, pp.123-129.
12. Z. Zainudin, M. Mohamed and M. R. Ramli, *The Malaysian Journal of Analytical Sciences*, 2010, **14(1)**, 24.