

# Mathematical Modelling Approach for Correlating Spectrophotometric Absorbance with Dissolved Oxygen

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**ABSTRACT:** A mathematical model has been developed in this paper for determination of dissolved oxygen (DO) in water samples by measuring the absorbance of monochromatic light by the sample. Determination of dissolved oxygen is an important parameter in the study of water quality. Winkler's method, based on titrations, is well established as the standard method for the determination of the DO. Experimentation was carried out to measure the dissolved oxygen and the absorbance of the water samples. Mathematical modelling has been carried out for determining DO values as a function of the absorbance observed for the samples. The correlation between absorbance of monochromatic light by the sample and DO values was determined. This correlation coefficient was found using curve fitting tools in the MATLAB software. Finally, the DO values hence obtained were compared with and found to be in close agreement with those obtained by Winkler's method.

**KEYWORDS:** Dissolved oxygen, correlation, Spectrophotometric absorbance, Biochemical oxygen demand, Mathematical modelling.

## I. INTRODUCTION

Dissolved Oxygen (DO) levels in natural waters and wastewaters depend on physical, chemical and biological activities in water body. The solubility of atmospheric oxygen in fresh water ranges from 14.6 ppm at 0°C to about 7.0 ppm at 35°C under normal atmospheric pressure. Natural water requires 5-6 ppm DO to support diverse ecosystem. Determination of dissolved oxygen is important for the study of water quality, sewage treatment and in precipitation and dissolution of inorganic substances in water. Analysis of DO is a key test in sanitary engineering practice. Determination of biodegradable organic substances in waste water has significant impact on the environmental pollution control. Measurement of biochemical oxygen demand (BOD) is important to keep check on the level of water pollution. The solubility of atmospheric oxygen in fresh water ranges from 14.6 mg/L at 0°C to about 7.0 mg/L at 35°C under one atmospheric pressure at any given temperature. It is necessary to know DO levels to assess quality of raw water and determine BOD. In liquid waste the dissolved oxygen is the factor that determines whether the biological changes are brought out by aerobic or anaerobic organisms. The DO measurement is used for calculation of BOD to determine the relative oxygen requirements of waste water, effluents and polluted waters. These tests measure the molecular oxygen utilized during a specified incubation period for the biochemical degradation of organic material and oxygen used to oxidize inorganic materials such as sulphide and ferrous ions. In standard practice, it is kept as 5 days [1].

## II. STATE OF ART

Conventional titrimetric methods are considered to be standard practice to estimate the BOD. However, with advancement of technology many sensor and biosensors have been developed to calculate the same. Mathematical

# International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 3, Issue 7, July 2014

models based on different parameters are being developed to calculate or estimate BOD from the sensed parameters of these sensors.

Data based modelling methods can be basically classified as follows:

1. Classical /Standard method
2. Chemical Kinetics based methods
3. Dispersion Models based methods
4. Emission Spectra based methods
5. Current/ Voltage based methods

### 1. Classical / Standard Methods

The method of determining DO by titration for different levels of dilution of water samples is the classical standard method for BOD measurement, known as Winkler’s method. This method is based on the fact that the oxygen present in a water sample rapidly oxidizes the dispersed divalent manganous hydroxide to its higher valency which precipitates as a brown hydrated oxide after addition of NaOH and KI. Upon acidification, manganese reverts to divalent state and liberates iodine from KI equivalent to the original DO content. The liberated iodine is titrated against  $\text{Na}_2\text{S}_2\text{O}_3$  (N/80) using starch and an indicator. Ferrous ion, Ferric ion, nitrite, microbial mass and high suspended solids constitutes the main sources of interference in this method, so many modifications in the estimation procedure to reduce these interferences are also used. It includes Alsterbergazide modification, Rideal Stewart Modification, Alum flocculation Modification and Alkaline Hypochlorite modification [1].

A recent modification of the standard method was suggested by Xinglong et al. in 2005 [2]. They proposed that the sample should be aerated upto the  $\text{O}_2$  concentration of about  $8 \text{ mg O}_2.\text{dm}^{-3}$  and incubated for definite time. When oxygen concentration decreased drastically, the sample was aerated again to similar concentration. The procedure was repeated in the next five days. In this way, owing to aeration the oxygen conditions were preserved at the desired uniform level during the time period of test. The total  $\text{BOD}_5$  was estimated by adding up the use of oxygen in the individual states.

### 2. Chemical Kinetics based methods

Siwiec et al. [3] has described the different approaches wherein researchers have experimented with the selected microorganisms to examine the decomposition of the organic compound and to control the kinetic of the oxygen used. The changes in the oxygen concentration in the surface water are described by the equation of Streeter and Phelps and they depend on saturation reaeration and changes in concentration of the contaminations. Modelling of BOD by the chemical kinetics employs equations of half order, first order and second order reaction. This was studied by Adrain and Sanders in their papers published in the duration 1992-1998 [4,5]. The following first order equation is frequently used to model the change of BOD with time.

$$\frac{dy}{dt} = k \cdot y \tag{1}$$

It is also often represented in the alternative form given in the following equation

$$\frac{d(L-y)}{dt} = k \cdot (L - y) \text{ or } \frac{dy}{dt} = K \cdot (L - y) \tag{2}$$

where, y = BOD value at any time

L= total BOD

k, K= the constant associated with reactions

These equations were used by researchers to model BOD using different mathematical and many inferences were drawn. Sheehy in 1960 [6] tried to indicate the constant K using to result of the BOD measurement after the first 24-hour incubation, the next and so on. On analysing the result he found that K does not always have a constant value. It was proposed that if  $K_{1/5}=K_{2/5}=...=K_{8/5}$  taking  $K_{5/5}$  as reference there is reaction of first order. Fujimoto in 1964 [7] integrated the equation and obtained the following result.

$$\frac{L-y}{L-y_0} = e^{-K.t} = 10^{-k.t} \tag{3}$$

Constructing the dependence diagram y(t) in the function y(t+1) and obtained rectilinear dependence, which enables the indication of functional gradient and intersection of point of vertical axis and parameter k and L on their basis. The same case as studied by Sheehy was stated by Marske and Pokowski in 1972 [8], when  $K \leq 0.2$  and  $K_{1/5}=K_{2/5}=...=K_{8/5}$  there is a lag decomposition reaction. They have suggested use of second order model if  $k > 0.2$ .

Thomas in 1965 [9] suggested the function which allowed to model this dependence and developed it in the series form as follows:

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 7, July 2014

$$\left(\frac{1}{y}\right)^{\frac{1}{3}} = \frac{1}{(2.3 \times k \times L)^{\frac{1}{3}}} + \frac{(2.3 \times k)^{\frac{2}{3}}}{6 \times L^{\frac{1}{3}}} \cdot t \tag{4}$$

The graph between  $t$  and  $\left(\frac{1}{y}\right)^{\frac{1}{3}}$  give a linear function whose intersection points A and B are -used to calculate  $k$  and  $L$ .

Navone in 1960 [10] compared the instantaneous time measurement ( $t_i$ ) and BOD value  $y_i$  with the differentiated value of standard equation 1 as follows:

$$\frac{dy_i}{dt_i} = \frac{y_{i+1} - y_{i-1}}{t_{i+1} - t_{i-1}}$$

When plotted this also shows linear dependence. Moore et. al. in 1950 [11] elaborated the dependence diagram by use of two vertical axes, where one was marked with values  $\frac{\sum y}{\sum(t.y)}$ , and other was marked by  $\frac{\sum y}{L}$ . The horizontal axis was the constant of the reaction  $k$ . Separate plots were used for depicting BOD3, BOD5 and BOD7. Consequently,  $\sum y$  and  $\sum(y, t)$  was also calculated and values of  $k$  and  $\frac{\sum y}{L}$  were read from graph which allowed to calculation of  $L$ . This method also calculated the length of lag phase of the BOD growth as a function of Time. Mason et. al. in 2006 [12] have proposed the application of the double exponential model

$$y = L_1 \cdot (1 - e^{-k_1 t}) + L_2 \cdot (1 - e^{-k_2 t})$$

where,  $L_1$  and  $L_2$  indicate the total BOD relativity. Index 1 refers to the case where contamination decomposed very easily and very quickly and the index 2 the case where contamination decomposition was more difficult and slower.

### 3. Dispersion models based methods

Bhargava, et al. from 1999 [13] studied the mathematical models used to predict DO concentration are differential equations representing the transport of BOD absorbing organic matter and its impact on water sample DO. These mathematical models include the effect of advection, dispersion, decay of dissolved BOD and reaeration from atmosphere. This model is based on Streeter – Phelps chemical model and is of little value for accurate prediction of BOD and DO in polluted stream, as it does not account for BOD removal due to bioflocculation.

Velzet. al. in 1962 [14] added a factor  $\alpha$  to the BOD rate constant,  $k_1$ , of the exponential form, to the first order kinetics in order to account for the BOD removal through sedimentation. But this is neither rational nor scientific. The various dispersion models develop to date account for the BOD which is present entirely in the dissolved form and not the least in settleable form.

Bhargava et. al. from 1983-86 [15,16a, 16b] proposed a dispersion model that takes into account the bioflocculated sedimentation, as well as biochemical decay of nonsettleable BOD. A numerical model was also proposed using an alternative finite difference scheme to model the BOD-DO balance under the stated condition in a stream which is free from numerical dispersion. The size of settleable particles is bigger than ionic size of soluble BOD causing material. The settleable part of BOD would not therefore be transported through diffusion. The effect of advective forces has been considered and included in the transition  $T_s$ . It is greater than the mixing time  $B_s$  the settleable part of BOD is removed by a linear settling law.

$$B_s = B_{o-s} \left[ 1 - \frac{V}{d} \tau \right], \tau \leq T_s \tag{5}$$

$$= 0, \tau > T_s$$

Where,  $B_{o-s}$  = initial settleable BOD

$V$  = settling velocity of particles

$D$  = Depth of stream

$\tau$  = time taken to travel a distance  $x$  from the source

The BOD concentration for the settleable part at any time  $t$  at a particular distance would depend on the settleable BOD situated at the outfall time earlier. The following expression is suggested as:

$$B_s(x,t) = B_{o-s}(0, t - \tau) \left[ 1 - \frac{V}{d} \tau \right], \tau \leq T_s \tag{6}$$

$$= 0, \tau > T_s$$

Since BOD is decaying exponentially with time the transportation equation of dissolved part is given. To show the effect of sedimentation of BOD on DO two cases were considered. The first case where the entire BOD in the source is in dissolved form while in the second case a part of total BOD is in settleable form. The total BOD in both cases is considered to be decaying exponentially with rate with respect to time at the outfall itself. This model describes

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 7, July 2014

the actual situation of domestic sea wage discharge into rivers through sewers. The model was developed to account for the feature therefore the prediction reflects a more rational quality profile of river. The combined effect of settle able and dissolved parts of BOD and DO is shown by a hypothesized approach. But rational data is used to show the effect due to non-availability of field data.

#### 4. Emission Spectra based methods

The growing need for online monitoring is resulted in the development of instrumentation based upon the variability in the absorption of light of waste water and natural waters. The technology based on fluorescence detection for the real time, non-invasive monitoring of biodegradable constituents of various sewage samples were studied by Reynolds in 1997 [17]. They studied and established a correlation between the UV absorbance at 254nm and the dissolved organic matter in natural water. Raw Sewage sample was studied for the fluorescence emission spectra. It showed that the inline band of emission at 340nm and treated effluent showed smaller maxima at 340nm and 450nm. Water Raman lines were used as internal intensity standards. Regression analysis of the fluorescence and BOD data and absorbance/BOD gave correlation coefficients. The lower regression coefficients of the FL/BOD over ABS/BOD was explained by introduction of errors from the normalization procedure and separation of water Raman line from fluorescence background. Implementing such a system to water waste processing plants could allow on line processing and control and lead to a reduction in operating cost. However the effect of environmental parameters on the validity of such correlation still needs to be investigated.

#### 5. Current/ Voltage change based methods

Vellinget al. [18] have studied the Clark type oxygen sensor and designed a sensor which is based on the diffusion limited amperometric oxygen sensor and a biomembrane. Steady state response and dynamic change of response is studied in this approach to measure the oxygen level. The working principle of these sensors described as follows: Substrate from the test media into which the sensitive biosensor is immersed in metabolized by microorganisms containing oxygen in the biomembrane of the sensor. This leads to redistribution of oxygen fluxes and causes decrease of the concentration of the oxygen at the oxygen sensor membrane, leading to decrease in the biosensor output sensor. As in the non-steady state regime the flux of oxygen towards the cathode is not proportional to the oxygen concentration in the biomembrane layer, the response, the lag time and process in biomembrane are given by the transfer function.

$$H^*(t) = \exp\left(-\frac{t}{T_s}\right) - 2 \sum_{n=1}^{\infty} (-1)^n X \frac{T_d}{n^2 T_s - T_d} \left[ \exp\left[-\frac{t}{T_s}\right] - \exp\left[-n^2 \cdot \frac{t}{T_d}\right] \right] \quad (7)$$

where,  $T_d$  and  $T_s$  are in time constant for oxygen sensor and for the exponential decay to oxygen concentration at oxygen sensor membrane. Linear dependence of  $T_s$  vs. Calibration solution concentration can be used for BOD sensor calibration.

### III. METHODOLOGY

Experimentation was carried out to study the correlation between absorbance of monochromatic light and amount of dissolved oxygen by using the sample water from various stages of Salawas Solid waste treatment plant situated near Jodhpur. The oxygen consumed in a 5 day BOD test period was measured by continuous oxygen uptake (Winkler's method) and UV absorption method (DR 500 Spectrophotometer) for DO and absorbance measurement. Samples were tested with many variations including using different dilutions and volume of sample.

Water samples were prepared in 30mL of solution in glass stopper bottle. The volume was selected after the studies done by the author to reduce the sample volume from 300 mL to 30 mL. Now, add 0.2 mL of 2.37M  $MnSO_4$  with the help of pipette followed by 0.2 mL of 12.5N alkaline-iodide-azide reagent in such a way that the tip of pipette should dip below the liquid surface while adding the reagents. Stopper the bottle immediately and mix well by inverting bottle 3-4 times. Allow to stand for 5 minutes, add 0.1mL of conc.  $H_2SO_4$  insert the stopper and mix well till the precipitate goes into solution and a yellow colour is obtained. This solution was used to determine DO by Winkler's titrimetric method and by measuring the absorbance at 380 nm using DR-5000 spectrophotometer. This wavelength was also chosen after doing the Spectrum study of the prepared samples after incorporating the reagents as described above. The maximum absorbance was observed at 380nm. The DO and the absorbance values obtained showed a decreasing trend.

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 7, July 2014

The DO values were normalized by dividing each reading of DO by the max. DO for that particular day (Blank data value of DO for that day). Similarly absorbance was normalized by dividing each reading of absorbance by the maximum absorbance for that particular day (Blank data value of absorbance for that day). The normalized data were further analysed using the Data modelling software MATLAB 7.0.0 (R2010a). MATLAB provides a curve fitting toolbox which is an interactive environment for fitting curves to 1-D data. The function cftool opens curve fitting toolbox with predictor data (x data) and the response data (y data). The linear polynomial fitting was used for the curve fitting. The acceptability of the fitted resultant curve was determined by calculating goodness of fit (gof) structure. gof structure has following fields [19]:

1. SSE (sum of squares of errors)

It is a statistic that measures the total deviation of the response values from the fit to the response values. It is also called the summed square of residuals and is usually labelled as SSE.

$$SSE = \sum_{i=1}^n w_i (y_i - \hat{y}_i)^2 \tag{8}$$

A value closer to 0 indicates that the model has a smaller random error component, and that the fit will be more useful for prediction.

2. R-square (coefficient of determination)

R-square is the square of the correlation between the response values and the modelled values. It is also called the square of the multiple correlation coefficient and the coefficient of multiple determination. R-square is defined as the ratio of the sum of squares of the regression (SSR) and the total sum of squares (SST). SSR is defined as:

$$SSR = \sum_{i=1}^n w_i (\hat{y}_i - \bar{y})^2 \tag{9}$$

SST is also called the sum of squares about the mean, and is defined as:

$$SST = \sum_{i=1}^n w_i (y_i - \bar{y})^2 \tag{10}$$

where,  $SST = SSR + SSE$ .

Given these definitions, R-square is expressed as:

$$R\text{-square} = \frac{SSR}{SST} = 1 - \frac{SSE}{SST} \tag{11}$$

R-square can take on any value between 0 and 1, with a value closer to 1 indicating that a greater proportion of variance is accounted for by the model

3. DFE (degree of freedom)

This statistic uses the R-square statistic defined above, and adjusts it based on the residual degrees of freedom. The residual degrees of freedom is defined as the number of response values n minus the number of fitted coefficients m estimated from the response values.

$$v = n - m \tag{12}$$

where, v = the number of independent pieces of information involving  
n = data points that are required to calculate the sum of squares.

4. RMSE (root mean square error)

This statistic is also known as the fit standard error and the standard error of the regression. It is an estimate of the standard deviation of the random component in the data, and is defined as

$$RMSE = s = \sqrt{MSE} \tag{13}$$

Where, MSE is the mean square error or the residual mean square

$$MSE = \frac{SSE}{v} \tag{14}$$

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 7, July 2014

Just as with SSE, an MSE value closer to 0 indicates a fit that is more useful for prediction. A curve with low rmse value was chosen as the best fitting curve.

The data was analysed using different fitting approaches such as Gaussian, Interpolant, polynomial and rational. The linear polynomial fitting was done using 1<sup>st</sup> degree, 2<sup>nd</sup> degree, 3<sup>rd</sup> degree and 4<sup>th</sup> degree polynomials. The best results were obtained for the 2<sup>nd</sup> degree polynomial functions. The function used for fitting of polynomials was polyfit (x,y,n) and that for its evaluation at the selected test points in polyval [p,x,s] . The function polyfit can be called as:

$$[p,s] = \text{polyfit}(x,y,n) \tag{15}$$

where, p= polynomial coefficients  
 s= structure for estimating errors  
 x= predictor data  
 y= response data  
 n= degree of polynomial.

The polyfit function finds the coefficient of a polynomial p(x) of degree n that fits the data p(x(i)) to y(i) in a least square sense. The result p(x) is of length n+1 containing the polynomial coefficient in descending powers and n is the degree of polynomial [20].

$$P(x) = p_1x^n + p_2x^{n-1} + p_3x^{n-2} + \dots + p_nx + p_{n+1} \tag{16}$$

The polyfit function also returns a structure S which is used with polyval function to predict error estimates. The polyval(p,x) returns the value of the polynomial of degree n evaluated at x. The coefficients in p are least square estimates as computed by polyfit. The error in the input data is considered to be independent normal and has constant variance.

The function polyval can be called as

$$[y,\text{delta}] = \text{polyval}(p,x,s) \tag{17}$$

where, y= value of polynomial p evaluated at x

delta = estimate of standard deviation of error in predicting an expected value of x by p(x),

p = polynomial coefficient

x = predictor data

s = structure as calculated by polyfit.

The correlation coefficients are calculated by using the correlation formula R= corrcoef(x). It returns a matrix R of correlation coefficients calculated from an input matrix X whose rows are the observations or the predictor data [20]. The corrcoef(x) is related to covariance matrix by

$$R(i,j) = \frac{C(i,j)}{\sqrt{C(i,i)C(j,j)}} \tag{18}$$

In the resultant matrix the rows represent the predictor data and the column represent response data. The diagonal elements are equal to 1.

### IV. APPLICATION AND RESULTS

The water samples procured from Solid Waste Treatment Plant,Salawas, Jodhpur, were studied by applying the proposed given in methodology and the DO obtained by Winkler's method and Absorbance Model are shown in Table1.

**Table 1. Observed and Normalized DO and Absorbance values**

| Sample | Dilution Water | % of sample used | DO using Winkler's technique |      | Absorbance at 380 nm light |       | DO (Normalized) |       | Absorbance (Normalized) |       |
|--------|----------------|------------------|------------------------------|------|----------------------------|-------|-----------------|-------|-------------------------|-------|
|        |                |                  | DO1                          | DO5  | Abs1                       | Abs5  | DO1n            | DO5n  | Abs1n                   | Abs5n |
| 0      | 300            | 0.00             | 7.12                         | 7.00 | 3.316                      | 3.316 | 1.000           | 1.000 | 1.000                   | 1.000 |
| 1      | 299            | 0.33             | 6.90                         | 6.75 | 3.256                      | 2.958 | 0.969           | 0.964 | 0.982                   | 0.892 |
| 2      | 298            | 0.67             | 6.75                         | 6.42 | 3.095                      | 2.878 | 0.948           | 0.917 | 0.933                   | 0.868 |

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 7, July 2014

|    |     |       |      |      |       |       |       |       |       |       |
|----|-----|-------|------|------|-------|-------|-------|-------|-------|-------|
| 3  | 297 | 1.00  | 6.67 | 6.19 | 3.055 | 2.55  | 0.937 | 0.884 | 0.921 | 0.769 |
| 4  | 296 | 1.33  | 6.60 | 6.01 | 3.054 | 2.893 | 0.927 | 0.859 | 0.921 | 0.872 |
| 5  | 295 | 1.67  | 6.59 | 5.02 | 3.04  | 2.458 | 0.926 | 0.717 | 0.917 | 0.741 |
| 6  | 294 | 2.00  | 6.55 | 5.08 | 3.014 | 1.936 | 0.920 | 0.726 | 0.909 | 0.584 |
| 7  | 293 | 2.33  | 6.50 | 5.44 | 2.963 | 2.58  | 0.913 | 0.777 | 0.894 | 0.778 |
| 8  | 292 | 2.67  | 6.47 | 5.82 | 2.943 | 2.921 | 0.909 | 0.831 | 0.888 | 0.881 |
| 9  | 291 | 3.00  | 6.36 | 5.45 | 2.861 | 2.611 | 0.893 | 0.779 | 0.863 | 0.787 |
| 10 | 290 | 3.33  | 6.30 | 4.75 | 2.827 | 1.884 | 0.885 | 0.679 | 0.853 | 0.568 |
| 11 | 289 | 3.67  | 6.28 | 4.56 | 2.797 | 1.773 | 0.882 | 0.651 | 0.843 | 0.535 |
| 12 | 288 | 4.00  | 6.22 | 4.54 | 2.76  | 2.104 | 0.874 | 0.649 | 0.832 | 0.634 |
| 13 | 287 | 4.33  | 6.03 | 3.75 | 2.745 | 1.884 | 0.847 | 0.536 | 0.828 | 0.568 |
| 14 | 286 | 4.67  | 6.04 | 3.66 | 2.666 | 2.55  | 0.848 | 0.523 | 0.804 | 0.769 |
| 15 | 285 | 5.00  | 5.85 | 3.56 | 2.655 | 2.151 | 0.822 | 0.509 | 0.801 | 0.649 |
| 18 | 282 | 6.00  | 5.75 | 3.46 | 2.543 | 1.537 | 0.808 | 0.494 | 0.767 | 0.464 |
| 21 | 279 | 7.00  | 5.39 | 2.94 | 2.474 | 1.11  | 0.757 | 0.420 | 0.746 | 0.335 |
| 24 | 276 | 8.00  | 5.03 | 2.82 | 2.253 | 0.056 | 0.706 | 0.403 | 0.679 | 0.017 |
| 27 | 273 | 9.00  | 4.82 | 2.62 | 2.127 | 1.061 | 0.677 | 0.374 | 0.641 | 0.320 |
| 30 | 270 | 10.00 | 4.70 | 2.6  | 1.612 | 0.025 | 0.660 | 0.371 | 0.486 | 0.008 |

Graph between DO and percentage sample used were plotted for day 1 and day 5. Similarly curve between absorbance and percent sample used plotted for day1 and day 5. A decreasing trend was observed. Percentage sample and absorbance versus percentage sample for day 1 and day 5. As the graphs were plotted for the observed set of data, therefore the results obtained will hold good for the given data set only. To overcome this problem the data set was normalized.

Using the normalized value 2<sup>nd</sup> degree polynomial functions were obtained for day 1 and day 5, as shown below

$$DO1n' = (-0.6073 * Abs1n^2) - (0.1597 * Abs1n) + 0.5646 \tag{19}$$

$$DO5n' = (0.7107 * Abs5n^2) - (0.0588 * Abs5n) + 0.3796 \tag{20}$$

Where DO1n' and DO5n' are the normalised values of DO obtained by using the mathematical model. The final values of DO are calculated by multiplying the DO1n' and DO5n' by the normalisation factors defined earlier. Finally, DO1' and DO5' are hence obtained as modelled values of DO from absorbance as shown in Table 2. The modelled values and the calculated values are plotted using plot function as shown in figure1 a,b. for day 1 and day 5, respectively.

**Table 2: DO values obtained from the model**

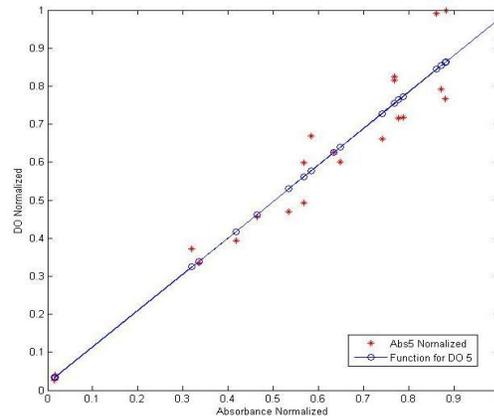
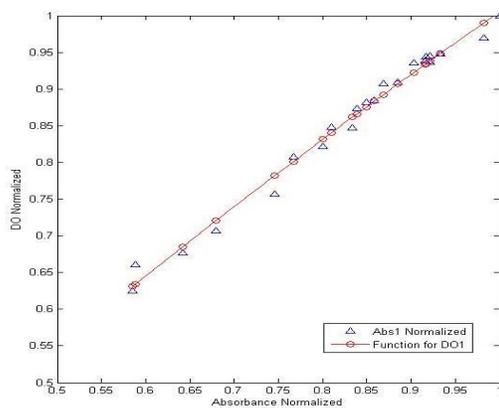
| Sample | Dilution Water | % of sample used | DO1n'  | DO5n'  | DO1'  | DO5'  |
|--------|----------------|------------------|--------|--------|-------|-------|
| 0      | 300            | 0.00             | 0.977  | 0.9972 | 6.956 | 6.980 |
| 1      | 299            | 0.33             | 0.9683 | 0.9592 | 6.894 | 6.714 |
| 2      | 298            | 0.67             | 0.9592 | 0.9212 | 6.829 | 6.448 |
| 3      | 297            | 1.00             | 0.9502 | 0.8855 | 6.765 | 6.198 |
| 4      | 296            | 1.33             | 0.9411 | 0.851  | 6.700 | 5.957 |

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 7, July 2014

|    |     |       |        |        |       |       |
|----|-----|-------|--------|--------|-------|-------|
| 5  | 295 | 1.67  | 0.9316 | 0.7396 | 6.632 | 5.177 |
| 6  | 294 | 2.00  | 0.9221 | 0.7244 | 6.565 | 5.070 |
| 7  | 293 | 2.33  | 0.9125 | 0.753  | 6.497 | 5.271 |
| 8  | 292 | 2.67  | 0.9025 | 0.8226 | 6.425 | 5.758 |
| 9  | 291 | 3.00  | 0.8926 | 0.7549 | 6.355 | 5.284 |
| 10 | 290 | 3.33  | 0.8826 | 0.6663 | 6.284 | 4.664 |
| 11 | 289 | 3.67  | 0.872  | 0.6392 | 6.208 | 4.474 |
| 12 | 288 | 4.00  | 0.8617 | 0.624  | 6.135 | 4.368 |
| 13 | 287 | 4.33  | 0.8512 | 0.5199 | 6.060 | 3.639 |
| 14 | 286 | 4.67  | 0.8402 | 0.4983 | 5.982 | 3.488 |
| 15 | 285 | 5.00  | 0.8293 | 0.5446 | 5.904 | 3.812 |
| 18 | 282 | 6.00  | 0.7956 | 0.4859 | 5.664 | 3.401 |
| 21 | 279 | 7.00  | 0.7605 | 0.4378 | 5.414 | 3.064 |
| 24 | 276 | 8.00  | 0.7239 | 0.4004 | 5.154 | 2.802 |
| 27 | 273 | 9.00  | 0.686  | 0.3735 | 4.884 | 2.614 |
| 30 | 270 | 10.00 | 0.6466 | 0.3572 | 4.603 | 2.500 |



**Figure 1.a,b Modelled Values of DO and absorbance for day 1 and day 5**

Correlation Matrix for day 1  
 1.0000 0.9916  
 0.9916 1.0000

Correlation Matrix for day 5  
 1.0000 0.9496  
 0.9496 1.0000

The correlation matrix elements have values close to 1. It shows that there exists a good correlation between predictor and the response values of the absorbance and the DO. The modelling has been done for the dataset where the concentration of the seeding water varies from 0 to 33 ppm. From the modelling it is found that the absorbance and the dissolved oxygen are highly correlated.

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 7, July 2014

This modelling has been done for the dataset where the concentration of the seeding water varies from 0 to 33ppm. From the modelling it is found that the absorbance and the dissolved oxygen are highly correlated. The goodness of fit is indicated by small values of SSE and RMSE, which are 0.069 and 0.093 respectively for day 1 and 0.060 and 0.070 respectively for day 5. The R-square values for day 1 and day 5 are 0.718 and 0.937 indicating acceptability of the models.

This approach can be used to get DO value from absorbance data, without the need of titration and to calculate the BOD values faster. It can also be used in designing an instrumentation system that measures the intensity or the absorbance of the solution and converts it to the DO values which in turn calculates the BOD of the water samples, automatically.

## V. CONCLUSION

The values of DO as obtained from Winkler's method and spectrophotometric absorbance depicted a similar linear trend. Based on this modelling was done to determine the correlation between the DO and Absorbance. The results obtained by the modelling shows that the absorbance and the dissolved oxygen are highly correlated. This approach can be used to get DO value instantaneously without the need of titration and to calculate the BOD values faster. It can also be used in designing an instrumentation system that measures the intensity or the absorbance of the solution and converts it to the DO values which in turn calculates the BOD of the water samples, automatically. A microcontroller based automatic calibration system can also be designed for directly estimating BOD values by obtaining the values for 1<sup>st</sup> day and 5<sup>th</sup> day from their corresponding absorbance measurement. This is expected to help in development of portable and fast field testing equipment for BOD determination.

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