Mathematical Models for Overall Gas Transfer Coefficient Using Different Theories and Evaluating Their Measurement Accuracy

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Abstract—Oxygen transfer, the process by which oxygen is transferred from the gaseous to liquid phase, is a vital part of the waste water treatment process. Because of low solubility of oxygen and consequent low rate of oxygen transfer, sufficient oxygen to meet the requirement of aerobic waste does not enter through normal surface air water interface. Many theories have come up in explaining the mechanism of gas transfer and absorption of non-reacting gases in a liquid, of out of which, Two film theory is important. An exiting mathematical model determines approximate value of Overall Gas Transfer coefficient. The Overall Gas Transfer coefficient, in case of Penetration theory, is 1.13 time more than that obtained in case of Two film theory. The difference is due to the difference in assumptions in the two theories.

The paper aims at development of mathematical model which determines the value of Overall Gas Transfer coefficient with greater accuracy than the existing model.

Keywords—Theories, Dissolved oxygen, Mathematical model, Gas Transfer coefficient, Accuracy.

INTRODUCTION

TO transfer the large quantities of oxygen that are needed, additional interfaces are created by employing aeration process. The creation of additional interfaces enhances the rate of oxygen transfer so that the dissolved oxygen level gets raised to allow aerobic bacteria to reduce biochemical oxygen demand of the effluent. To provide the required amount of oxygen, an aeration system is always needed[1]. Many theories have come up in explaining the mechanism of gas transfer and absorption of non-reacting gases in a liquid, of out of which following are important. [2]- [3]

1. Two film theory
2. Penetration theory

Two Film Theory: This theory assumes that at the interface between a gas and a turbulent liquid, through which the gas must pass by the relatively slow rate of molecular diffusion.

In the case of gas of low solubility like oxygen in water, the gas film offers relatively little resistance. Hence,

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it may be assumed that the concentration of gas in solution at the interface is because of saturation and that the entire resistance to the passage of the gas into the liquid is due to the liquid film. Beneath the liquid film the gas in solution is assumed to be mixed with main body of the liquid at such a rate that the concentration can be taken as constant through out. It is stated in the theory that these films are only responsible for the resistance offered. It is further stated that turbulence can cause no effect on the existence of these films. It can at the most reduce the thickness of these films. When a gas is dissolved in water the process is generally treated as a mass transfer occupying over four relatively distinct steps. [4].The first step involves passage of the gas through the vapor phase to the gas liquid interface. The gas must pass through a 'gas film' on the vapor side of the interface in the second step of transfer and through the liquid film on the liquid side of the interface in the third step of transfer. Finally the gas must disperse through out the bulk of the solution. Each of these steps involves a finite increment of time. However, conditions generally will be such that of particular step will take the time so long relative to others that the rate for the remaining steps will be insignificant in the overall process. The step taking the longest time under given set of conditions is termed as the rate limiting step and the overall gas transfer rate calculation may be based on this step only.

If the quiescent or stagnant condition is maintained, diffusion of gas through out the bulk solution phase is generally the slowest step and under such conditions molecular diffusion expressions may be used to predict rate of transfer or increase of concentration of gas dissolved in the liquid as function of time.

If the solution phase is sufficiently agitated by natural turbulence or by induced mechanical mixing, bulk solution diffusion ceases to be rate limiting and rate transfer through the gas liquid interface becomes the controlling factor. The solubility of a particular gas in the solution phase will govern which of the two interfacial films limits the rate of transfer across the interface.

II. EXISTING MATHEMATICAL MODELS

A. Two Film Theory:

The basic equation for the rate of transfer of a gas in solution by molecular diffusion is given by Fick's law [5].

$$\frac{\partial m}{\partial t} = -D \frac{\partial c}{\partial x} \tag{1}$$

where,

$\partial m/\partial t$ = Rate of mass transfer in the direction of x across a unit cross a unit area normal.

$\partial c/\partial x$ = Concentration gradient.

If the concentration gradient also changing with x, the rate of transfer across a unit area at point (x+dx) is,

$$-D\left(\partial c/\partial x + \partial^2 c/\partial x^2 . dx\right)$$

The rate of gain of concentration within the element of volume dx is given by

$$\frac{\partial^2 m}{\partial x \partial t} = \frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad (2)$$

If the liquid film has a thickness L, the steady state rate of transfer across the film would be given [6] by

$$\frac{dm}{dt} = D.A\left(\frac{C_i - C_L}{L}\right)$$

$$= K_L.A(C_i - C_L) \qquad (3)$$

and the rate of change of concentration in the main body of the liquid is given as

$$\frac{dc_L}{dt} = K_L.\frac{A}{L}(C_i - C_L) \qquad (4)$$

Where,

C_L = Concentration in the body of liquid.

C_i = Concentration at the interface.

A = Area of interfacial contact.

V = Volume of liquid.

L = liquid film has a thickness

K_L = D/L is the overall gas transfer coefficient

From this it follows that

$$\log_e\left(\frac{(C_i - C_o)}{(C_i - C_L)}\right) = K_L.\left(\frac{A}{L}\right)t \qquad (5)$$

In which C_o is the initial concentration in liquid and (A/L) = a,

$$\text{Or} \quad K_L a.t = \log_e\left(\frac{(C_i - C_o)}{(C_i - C_L)}\right)$$

$$\text{Or } K_L a = \frac{\log_e(C_i - C_o) - \log_e(C_i - C_L)}{t_2 - t_1}$$

$$\text{Or } K_L a = \frac{\log_e U_1 - \log_e U_2}{t_2 - t_1}$$

$$\text{Or } K_L a = \frac{\log_e \dfrac{U_1}{U_2}}{t_2 - t_1}$$

$$K_L a = \frac{2.303 \log_{10} \dfrac{U_1}{U_2}}{t_2 - t_1} \qquad (6)$$

where U_1 and U_2 are under saturation concentrations in ppm at time t_1 and t_2 respectively.

Obviously, the measurement of the overall rate transfer coefficient $K_L a$ may be obtained by plotting these on semi log graph with saturation deficit on the long scale. Slope of the curve will give the value of $K_L a / 2.303$ and $K_L a$ can be calculated by multiplying the slope by 2.303.

B. Penetration Theory:

As per this theory eddies are originated in the turbulent bulk of liquid. These eddies come to the gas-liquid interface and are displaced by the other eddies arriving at the gas interface. However, before having displaced they come in contact with the gas in the near vicinity and absorb the molecules from the gas. These are redistributed in the liquid body by the returning eddies. According to this theory it has been assumed that the rate of transfer is a function of molecular diffusion coefficient 'D', Concentration gradient and surface renewal factor. [1] Higble who is the producer of this theory used the equations which were developed by Stefan.

If C is the concentration of the gas in the liquid at any time 't' at a depth x below the liquid surface, Ct is the average concentration of the gas at time 't' in any sample from the liquid body ,then Stefan defined the boundary condition as
C = C_t when t = 0, x > 0
C = C_s when t = 0, x = 0
Instantaneous rate of transfer of a gas across a unit area of interface is given by

$$N_i = (C_s - C_t)\sqrt{D/\pi.t} \qquad (7)$$

where,
D = diffusively in cm³/hr.
N_i = Instantaneous rate of transfer across the unit area of interface in ppm/hr
Total amount of gas carried across the interface during the interval of time 't' will be given by

$$\int_0^{t'} N_i = \int_0^{t'} (C_s - C_t) \sqrt{D/\pi . t}$$

$$= (C_s - C_t) \sqrt{D/\pi .} \int_0^{t'} t^{1/2} dt$$

$$= (C_s - C_t) \sqrt{D/\pi .} \left(\frac{t'^{1/2}}{1/2} \right)$$

Or

$$\int_0^{t'} N_i \, dt = 2(C_s - C_t) \sqrt{Dt'/\pi .} \tag{8}$$

But Average rate of transfer during the time t' equals the total amount transferred divided by 't'
Thus,

$$N = \frac{1}{t'} \int_0^{t'} N_i \, dt = 2 (C_s - C_t) \sqrt{Dt'/\pi .} \; \frac{1}{t}$$

Or

$$N = 2 (C_s - C_t) \sqrt{D/\pi t' .} \tag{9}$$

Where, N is the average rate of transfer across a unit area of interface during the time t'. In a turbulent body of liquid, t' is the time taken between formations and mixing of the film, i.e. time of existence of the interfacial layer. In this case the phenomena of mixing is very well compared with the situation where as the liquid remarked quiescent for infinitesiminal period of time t' and was mixed instantaneously and also this process being repeated indefinitely. The average rate of transfer will be given by the above equation as t' remains constant. If the time of renewal t' is replaced by rate of surface renewal then 1/t' = 1 equation (9) becomes:

$$N = \frac{2}{\sqrt{\pi}} (C_s - C_t) \sqrt{D. r}$$

$$N = 1.13 (C_s - C_t) \sqrt{D . r} \tag{10}$$

If this equation is compared with the equation (3) then

$$K_L a = 1.13 \sqrt{D . r} \tag{11}$$

In 1951, another important factor r' which is the average frequency with which any particular vertical element of the liquid is mixed was proposed by Danckwert as an important modification of the penetration theory. It was assumed that there was no correlation between the time of exposure of the vertical element of liquid to gas phase and its chances of being mixed across the area of the interface was completely random, It was obtained-

$$K_L a = (C_s - C_t) \sqrt{D . r'} \tag{12}$$

This given

$$K_L a = 1.13 \sqrt{D . r'} \tag{13}$$

The absorption coefficient $K_L a$ in equation (11) is 1.13 time than that obtained in equation (13). The difference is due to the difference in assumptions in the two theories.

The two film theory states when highly soluble non-reacting gas is transferred into water the resistance offered by vapor gas film for diffusion of gas through the vapor gas film should be taken into account .When exchange of dissolved gases with oxygen in water is required, resistance of both the films for both the gases should be considered for transfer of each gas and the predomination will be ascertained for each gas. All aeration system involves mixing of liquid and renewal of water surfaces. As such transfer of oxygen by the mechanism of molecular diffusion through the saturated interfacial films may not be significant. The instantaneous new saturated films are aerated when interfacial surface of liquid or gas is mixed and they are physically broken and mixed by the process of mixing into the main body of the liquid. Although the penetration theory and its modifications have considered the transfer into a mixing system but they do not really account for major portion of oxygen transferred into the lower main liquid body by breaking the film physically.

III. MATHEMATICAL MODEL

Oxygen transfer through water is governed by Fick's law of diffusion and is a liquid film controlled process [7]. Thus,

$$\frac{dm}{dt} = D_L . A . \frac{dc}{dy}$$

Or

$$\frac{1}{V} . \frac{dm}{dt} = \frac{dc}{dt} = (D_L . a)/(Y_L . V)(C_s - C_t) \tag{7}$$

Or

$$\frac{dc}{dt} = K_L . a (C_s - C_t) \tag{14}$$

Where,

$$\frac{dm}{dt} = \text{Rate of mass transfer by diffusion.}$$

V = volume of liquid.

$$\frac{dc}{dt} = \text{Rate of change in concentration with time.}$$

D_L = Diffusion coefficient of gas in the liquid.

Y_L = Liquid fill thickness through which diffusion occurs.

C_s = saturation concentration of gas in solution in mg/lit.

C_t = Concentration of gas in the bulk solution in mg/lit.

A = Cross sectional area through which diffusion occurs.

Separating the variables, Equation (14) becomes

$$\frac{dc}{(C_s - C_t)} = K_L.a.dt$$

Integrating, we get

$$-\ln(C_s - C_t) = K_L a.t + A \tag{15}$$

Where A is Constant of integration

At $t = 0$, $C_t = C_0$

Therefore, Equation (15) becomes

$$-\ln(C_s - C_t) = K_L.a^0 + A$$
$$A = -\ln(C_s - C_t)$$

Substituting the value of A in the equation (15)

$$-\ln(C_s - C_t) = K_L.a.t - \ln(C_s - C_0)$$

Simplifying,

$$\ln(C_s - C_t) - \ln(C_s - C_0) = -K_L.a.t$$

$$\therefore \ln(C_s - C_t)/(C_s - C_0) = -K_L.a.t$$

$$\therefore (C_s - C_t)/(C_s - C_0) = e^{-K_L.a.t}$$

$$\therefore (C_s - C_t) = (C_s - C_0)\ e^{-K_L.a.t}$$

Rearranging the above equation

$$C_t = C_s - (C_s - C_0)e^{-K_L.a.t} \tag{16}$$

Equation (16) can be written as

$$C_t = (C_s - C_0) - (C_s - C_0)e^{-K_L.a.t} + C_0$$

$$C_t = (C_s - C_0)(1 - e^{-K_L.a.t}) + C_0 \tag{17}$$

The Concentration of dissolved oxygen at time (t + h) can similarly be expressed as

$$C_{(t+h)} = (C_s - C_0)(1 - e^{-K_L.a(t+h)}) + C_0 \tag{18}$$

or

$$C_{(t+h)} = C_s - C_s(e^{-K_L.a(t+h)}) - C_0 + C_0(e^{-K_L.a(t+h)}) + C_0$$

$$C_{(t+h)} = C_s - C_s(e^{-K_L.a(t+h)}) + C_0(e^{-K_L.a(t+h)})$$

$$C_{(t+h)} = C_s - (e^{-K_L.ah}(C_s.e^{-K_L.at} - C_0.e^{-K_L.at}))$$

$$C_{(t+h)} = C_s - (e^{-K_L.ah}(C_s - C_0).e^{-K_L.at}) \tag{19}$$

But from equation (16)

$$(C_s - C_0).e^{-K_L.at} = (C_s - C_t)$$

Substituting this values in equation (19)

$$C_{(t+h)} = C_s - (e^{-K_L.ah}(C_s - C_t).)$$

Simplifying

$$C_{(t+h)} = C_s - C_s.e^{-K_L.ah} + C_t\,e^{-K_L.ah}$$

$$C_{(t+h)} = C_t\,e^{-K_L.ah} + C_s(1 - .e^{-K_L.ah}) \tag{20}$$

Thus equation (20) is comparable to an equation of straight line of the form

Y= m X + A

IV. RESULT AND DISCUSSION

The value $K_L a$ arrived at by equation (6) may be influenced by inaccurate assumption of saturation dissolved oxygen concentration (C_s) and truncation of re-aeration data at lower & higher end in estimation of initial oxygen concentration. A slight deviation in the assumption of C_s value results in a remarkable change in the nature of the curve. Any attempt to fit the straight line for this plot will involve some amount of inaccuracy in the $K_L a$ value.

Beside the truncation of data at lower end and higher end and discrepancies due to estimation of initial oxygen concentration, inaccuracy also results from error in locating the exact time (long period) after which re-aeration starts adding oxygen to water.

Therefore it is clear from above discussion that unless a correct value of C_s is assumed it is impossible to get a straight line plot between $\log_{10}(C_s - C_t)$ and Time, under these circumstances some error will always be associated with $K_L a$ value.The absorption coefficient $K_L a$ in equation (11) is 1.13 time than that obtained in equation (13). The difference is due to the difference in assumptions in the two theories.

Equation (20) indicates that the plot between $C_{(t+h)}$ and C_t should yield a straight line. The slope of this line (m)

represents the value of $e^{-K_L.ah}$ from which $K_L a$ can be calculated. Similarly the intercept on the Y- axis (A) represents the term $C_s\left(1 - . e^{-K_L.ah}\right)$ from which the value of C_s can be known. The main difference between the equation (6) and equation (14) is that, for former, the value of saturation dissolved oxygen concentration (C_s) is to be assumed but for later the plot itself provide the value of saturation dissolved oxygen concentration (C_s), thereby eliminating the assumption of C_s value and subsequently eliminating the error.

V. CONCLUSION

It can be finally concluded that,

1) Unless a correct value of C_s is assumed it is impossible to get a straight line plot between $\log_{10}\left(C_s - C_t\right)$ and Time while using equation (6) for Two film theory. If incorrect value is assumed, then the value of gas transfer coefficient determined will be inaccurate.

2) While using Penetration theory, equation (13) yields the value of overall gas transfer 1.13 times more than that of equation (6).

3) While using equation (20), since it is not based on any kind of assumptions, the value of gas transfer coefficient determined is more accurate. Therefore, equation (20) can be used with confidence for determining the value overall gas transfer coefficient.

REFERENCES

[1] Wesner, G.M., Ewing, J. J., Lineck, T.S.,Jr., and Hinrichs, D.J.1977. "Energy conservation in municipal wastewater treatment." EPA-130/9-77-011, NTIS No PB81-165391, U.S. EPA Res., Washington, D.C.
[2] O' Conner. D.J. " Biological waste Treatment". John Wiley & sons, Inc., New York. P.76.
[3] Metcalf and Eddy Inc. (2001). Waste water Engineering; Treatment disposal and reuse. Tata McGraw Hill. New Delhi, India.
[4]. Rich Linvil, G., (1961). "Unit operations of sanitary Engineering", John Wiley & sons, Inc. London, P.171.
[5] Enkenfelder, W.W.Jr, " Aeration and Mass transfer", Ind. Water pollution control, McGraw Hill Inc., p.65.
[6]. Fair, G.M., Gayer, J.C., (1976). "Water supply and Waste water disposal, John Wiley & sons, Inc., New York. P. 450.
[7] Rajkumar, (1991)." Oxygen Transfer through Mechanical Aeration". M.E. Thesis. University of Roorkee. Roorkee. India.

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