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Unification of The Oxygen Transfer Standards

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Abstract

Current application of clean water aeration test standards for wastewater treatment systems is based on the most commonly and internationally used standards for the clean water test, such as the ASCE(USA), CEN(EU/EFTA), and DWA(Germany). All the standards are mostly unified in respect to the methodology employed to calculate the oxygen mass transfer coefficient KLa, in the use of a non-steady state method or a variation of such; in the use of sulfite deoxygenation or a variation of such to give a zero starting point; in the use of probes or a variation of such to measure step change of dissolved oxygen concentration; and, in the use of the non-linear regression method of analysis or a variation of such to estimate the transfer parameters. But there are differences between the various standards, and therefore, there is a need to reconcile all the standards for the benefit of mankind. In particular, this paper addresses a problem common to all the standards, which is the application of clean water test result to in-process oxygen transfer rates, as a first step in the attempt of unifying the standards. In particular, this paper mainly applies to a diffused system but the proposed concept of gas-side oxygen depletion should be applicable to all kinds of aeration systems even for non-submerged aeration equipment.

Keywords: Wastewater Treatment, Activated Sludge, Mathematical Modelling, Oxygen Transfer, Standards

1. Introduction

Current application of clean water aeration test standards for wastewater treatment systems such as the ASCE(USA) standards, the European standards CEN(EU/EFTA), and the German standards DWA(Germany) are mostly unified in respect to the methodology employed to calculate the oxygen mass transfer coefficient KLa, and in their use of a non-steady state method and their associated details to calculate the clean water oxygen transfer rates. But there are differences between the various standards, and therefore, there is a need to reconcile all the standards for the sake of normalization. This paper specifically addresses a problem common to all the standards, which is the application of clean water test results to estimating process oxygen transfer rates, as a first step in the attempt of unifying the standards. In particular, this content mainly applies to a diffused system.

In the published standards, ASCE standard (ASCE 2022) (ASCE 2007) Standard 2-22, Standard 2-06, the clean water test (CWT) is based on a completely mixed system [1,2]. This system is idealized as completely-mixed in which oxygen is transferred throughout the volume with a dissolved oxygen concentration of C and an average overall mass transfer coefficient (KLa) being uniform throughout the volume. The main criticism of this method is that in the activated sludge process, the oxygenation mechanism is typically different from the CWT test standard situation. In an in-process situation, there is continual oxygen consumption and wastewater through-flow. For diffused aeration, the presence of surface-active agents inhibits molecular diffusion of oxygen through the gas-liquid interface and there is a decrease in surface renewal and so decreasing the rate of transfer compared to clean water. However, for mechanical surface aeration system, this effect is opposite since the high mixing intensities cause a high surface renewal and increase the surface contact areas associated with turbulent conditions. Formation of a large number of small droplets of water can substantially increase the contact areas resulting in a much higher oxygen transfer than in clean water, yielding KLa values as high as 1.2 times that of clean water [3].

In either case, the influent wastewater flow condition is typically plug-flow (i.e., only limited mixing is provided), with a progressive change of the effective viscosity along the flow length due to a change in surfactant concentration resulting in a change in surface

tension, as the degree of purification of the raw sewage/mixed liquor increases toward the end of the aeration basin.

The importance of mixing for the substrate (BOD and nutrients) removal and for the sludge characteristics is easy to imagine [4,5]. For the entire aeration basin, the resulting in-process KLa bears little resemblance to the KLa estimated from the CWT. In addition, the author postulated that the respiration from the metabolic activities in the microbial cells contribute to the obstruction of oxygen transfer during the flow-through journey of the sewage, making the transfer efficiency poor in the beginning but progressively improves as the treatment train progresses, so that taking the exit train prior to its effluent, the water quality is substantially purified, with the microbial cells nearing their endogenous state when the substrates are mostly consumed [6-8]. The influence of incomplete-mixing and challenges associated with acquiring mixing characteristics from the tests have been discussed in ASCE (2022). The effect of scaling of reactor volume, reactor configuration, and the method of aeration may be only partly discussed systematically. The discussions however, would help the reader to understand and appreciate the problem better and the complexity of calculating the oxygen transfer rate. The mass transfer coefficient therefore becomes substantially recovered compared to its clean water state, and the ratio of the respective KLa's becomes approaching closer to unity. According to the author, and for diffused aeration, the evaluation of KLa should also consider the microbial respiration effect, which then exerts a different gas-side oxygen depletion in the bubble stream as compared to clean water aeration, and this departure of the gas depletion rate from clean water must be accounted for in the basic oxygen transfer model.

The sewage flow train, from the initial primary treatment, to secondary treatment, to tertiary treatment, and finally to sludge treatment, representing treatment processes applicable for renovating wastewaters using current technology, typically requires proper design criteria predicated on bench or pilot plant scale tests. Oxygen transfer in the aeration basins is no exception. It is not possible to always test a system at full-scale, simply because full-scale is not available prior to a design. Therefore, the drawback of the current standards lies in the difficulty to facilitate testing under a reduced scale, and the lack of experimental procedures necessary for such formulations.

The use of the Damkohler (I) number Da for limited-mix reactors in CEN (2003) and DWA (2007) is questionable, as there are no chemical reactions in clean water oxygen transfer, and so the estimation of KLa for wastewater should be independent of this number [9,10].

2. Mechanism of Submerged Oxygen Transfer

One of the major conflicts between the ASCE standard and the European standards is the mathematical treatment on the dissolved oxygen saturation concentration C* in the CWT. ASCE (2007) stipulate volumetrically and depth-wise representative sampling as the only method of arriving at the global saturation value, further supported by Jiang and Stenstrom (2012). CEN (2003) propose the effective depth ratio (de/Zd) to be 50% for a theoretical calculation of the saturation concentration to avoid the need for accurate DO probe calibration, if agreed between the parties concerned. While referring to this, DWA (2007) put forward 40% to 50%, unless depth is greater than 7m, for which 33% is stated. For a 6m diffuser submergence, assuming 50% where 33% would be detected by testing, an overestimate of SOTR by 8% results, a considerable bias. The empirical approach in the ASCE standard appears to be the only reasonable way to obtaining the global saturation value, or equivalently, the effective submergence de. [Uby 2019] Unfortunately, the empirical approach cannot determine the equilibrium concentration under a respiring setting. The relationship between KLa and C* (DO saturation concentration) is not fully understood in any of the standards. These two functions are in fact intimately related. They are inversely proportional to each other under controlled conditions [11,12]. When the water molecules are bonded as a liquid medium, the inter-molecular forces can change according to environmental conditions. When these bonds are weakened, gas can more easily enter the interstitial spaces between the water molecules in the liquid and so the rate of gas transfer as exemplified by the KLa parameter increases. At the same time weakened forces between the water molecules mean that the water cannot hold as much gas molecules entering the system, and so the solubility of the gas decreases. A simple experiment in a beaker of water would illustrate the fact. If the beaker is initially devoid of dissolved oxygen when subjected to oxygen dissolution by diffusion, the amount of oxygen transfer is the product of KLa and C* over the beaker volume. This product is a constant no matter how the intermolecular forces change, as can be illustrated by changing the water temperature (within the normal working range) that would affect the kinetic energy that would change the forces [13-15]. The initial rate of transfer is therefore given by $dC/dt = C^*.KLa$. This is the standard model of oxygen transfer in its most basic form.

When the author refers to "oxygen depletion in the gas bubble" in a respiring system, he means the oxygen consumption R by the microbes because of the mass balance as shown in the mole fraction variation curves in Figure 1, i.e., R is the difference in the exit gas of a clean water and the exit gas of a respiring water, all at their respective steady states. If this is the case, first the oxygen will be consumed from the liquid phase before it is then transferred from the gas bubble to the liquid phase. This mechanism could be mentioned here for the sake of more clarity but may not be true. Like any physics problem, the principle of superposition would be a better mechanism as it is a powerful tool in tackling such problems as oxygen transfer in an aqueous solution where many different forces are at play simultaneously. As the dissolved oxygen content builds up in an aeration basin, this build-up of dissolution gas in the aqueous solution exerts a counter-force in favour of diffusing of the DO molecules from the liquid to the gas phase. When the principle of superposition is applied to the system, the net rate of oxygen transfer between the aqueous phase and the gas phase is the vector sum of the two opposing forces, depending on which force is predominantly stronger. In mathematical form, therefore, the net transfer is given by $dC/dt = KLa \sum c$, where 'c' ranges from

zero to C*. This can be written as dC/dt = KLa (C* – C) assuming the liquid film coefficient does not change regardless of whether the gas molecules are going into or out of the bubble, and both C* and Care time-dependent variables.

3. Le Chatelier's Principle Applied to Gas Transfer

Conceptually, before reaching the saturation state in a non-steady state test, since the oxygen concentration in the water is less than would be dictated by the oxygen content of the bubble, Le Chatelier's principle requires that the process in the context of a bubble containing oxygen and rising through water with a dissolved-oxygen deficit, relative to the composition of the bubble, would seek an equilibrium via the net transfer of oxygen from the bubble to the water [16]. In this scenario, as shown in Figure 1, even for the ultimate steady-state (SS), oxygen goes in and out of the gas stream depending on position and time of the bubble of the unsteady state test. In clean water, one can view the mass balances as having a two-way transfer---one way by diffusion into water; and the other by diffusion from the water back to the gas stream which serves as the reverse sink. Whichever is the greater transfer rate would depend on the magnitude of the driving forces one way or the other. At system equilibrium, these two rates are the same at the equilibrium point of the bulk liquid, the equilibrium point being defined by the effective depth 'de' in ASCE standard 2-22.

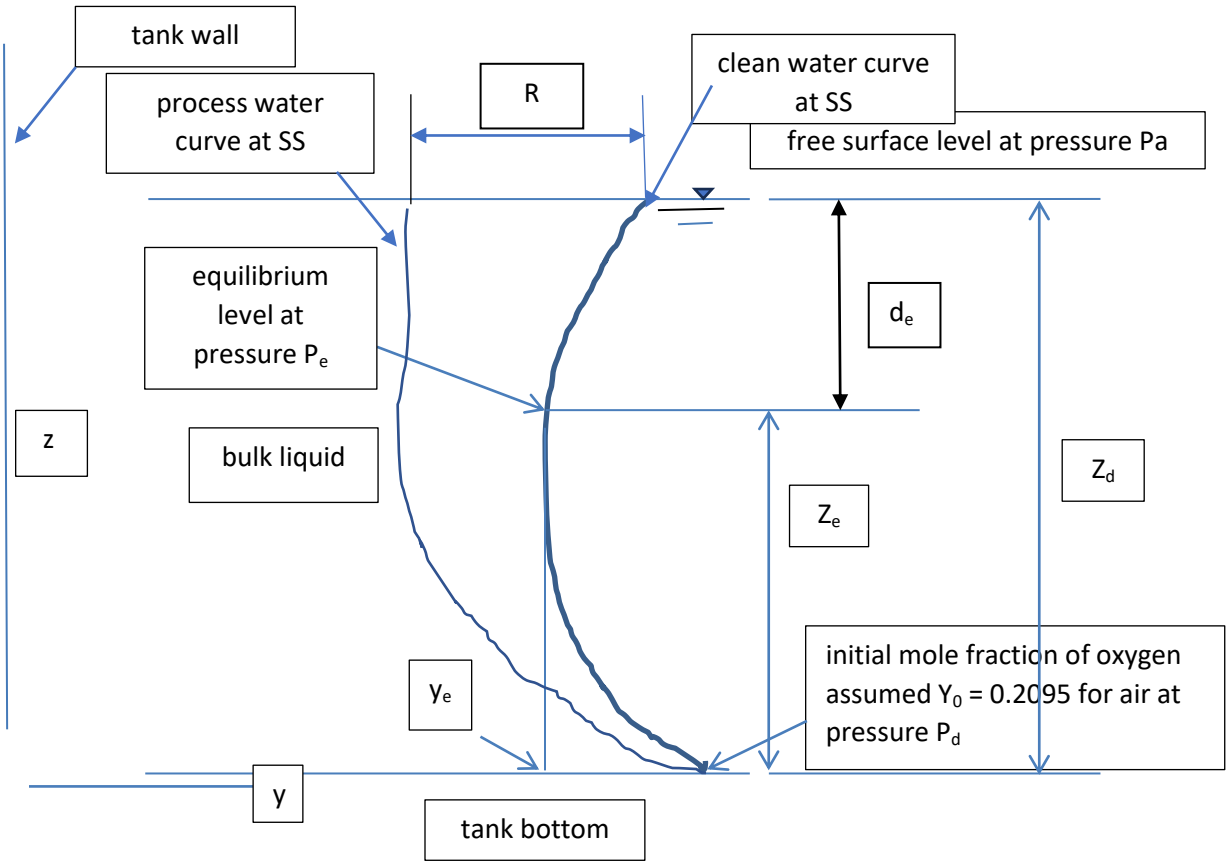

Figure 1: Oxygen Mole fraction curve at saturation for the Lee-Baillod model [Eq. 3] (subscript e = equilibrium) [Lee 2018]

At steady state (SS), the entire system is then in a dynamic equilibrium, with gas depletion in the bubble at the lower half of the tank below the 'd_e' level, and gas absorption back to the gas phase above de; the two movements balancing each other out.

Therefore, the general understanding that: "T*he overall mass transfer coefficient "*$K_L a$*" incorporates the mass transfer through the gaseous and liquid films at equilibrium*", is applicable to clean water only, equilibrium being normally defined as a state where the gas flowing into the *bulk liquid* equals the gas flowing out of the *bulk liquid*. Equilibrium means the fugacity of the oxygen in the gas phase is equal to the fugacity of the oxygen in the liquid phase [17]. LeChatelier's principle applies to equilibrium. If the system is in equilibrium, then it is at steady state, and shown in Figure 1 as a mole fraction variation curve at clean water saturation.

In contrast, the oxygen mole fraction (the ratio of the oxygen mass content to the entire mass content of a bubble) varies with the bubble location in a wastewater aeration basin, and will be represented by another variation curve for any in-process water oxygen transfer and will not reach equilibrium even at steady state (SS), as shown in the same figure as a different curve for process water. Steady-state (SS) does not mean equilibrium, but equilibrium does mean SS.

The standard mass transfer model for a bulk liquid aeration under constant gas flow rate has been theoretically derived [Lee 2018] repeated herewith as eq. 1:

$$\frac{dC}{dt} = K_L a\,(C^*_{\infty} - C) \tag{1}$$

where C^*_{∞} is the ultimate steady-state equilibrium dissolved oxygen concentration in a non-steady state CWT.

In Lee [2018], a model has been developed for the mole fraction variation curve and is defined as the Lee-Baillod model. The model, and the subsequent integrated form, was based on a constant bubble volume and was therefore named the constant bubble volume model (CBVM). For the more general case, where the bubble size is a variable, exacerbated by gas-side gas depletion, the mole fraction variation curve is based on the generalized Lee-Baillod equation (Eq. 3) which the author derived by assigning calibration factors (n, m) where appropriate to the Lee-Baillod equation, and it can be subjected to mathematical integration just like for the CBVM.

All the resulting equations that lend themselves to five simultaneous equations (eq. 2 to eq. 6) for solving the unknown parameters (n, m, K_La_0, y_e, Ze) are reiterated and summarized below:

$$K_L a = \frac{[1 - \exp(-K_L a_0\, x\,(1-e)Z_d)]}{x(1-e)Z_d} \tag{2}$$

$$y = \frac{C}{nHP} + \left(\frac{Y_0\,P_d}{P} - \frac{C}{nHP}\right)\exp(-xK_L a_0.mz) \tag{3}$$

$$C^*_{\infty} = nH(0.2095)\frac{P_a - P_d\exp(-mx.K_L a_0.Z_d)}{1-\exp(-mx.K_L a_0.Z_d)} \tag{4}$$

$$K_L a = \frac{1-\exp(-mx.K_L a_0.Z_d)}{nmx.Z_d} + \frac{(n-1)K_L a_0}{n} \tag{5}$$

$$Z_e = \frac{1}{mxK_L a_0}\left\{\ln\left(P_e\frac{mxK_L a_0}{nr_w}\right) + \ln\left(\frac{nHY_0P_d}{C^*_{\infty}} - 1\right)\right\} \tag{6}$$

where x = HR'T/Ug where Ug is the height-averaged superficial gas velocity; H is Henry's Law constant; R' is the specific gas constant of oxygen (note: a different symbol is used to distinguish it from the respiration rate R); T is the water temperature in Kelvin; *e* is the effective depth ratio e = d_e / Z_d. Hence, with the above suite of equations, the basic transfer equation for the non-steady state clean water test as given by eq 1, is proven valid for the general case (non-constant bubble volume) as well, where $K_L a$ and C^*_{∞} are obtainable by solving the above set of equations when the baseline K_La_0 is known. The concept of a baseline or a benchmark for the mass transfer coefficient was given by previous papers published by the author.

Based on the above derivation, by the principle of mathematical induction, it can be argued that, for very shallow tank ($Z_d \approx 0$), the basic transfer equation is again applicable, hence, the following equation would apply:

$$\frac{dC}{dt} = K_L a_0\,(C_S - C) \tag{7}$$

Where Cs is the handbook solubility value at the atmospheric pressure and water temperature at testing. Comparing Eq. (1) with Eq. (7), the two mass transfer coefficients are not the same, since the former has incorporated the effect of gas depletion as seen in the derivation (Lee 2018), whereas in the latter equation, gas depletion is non-existent because of the hypothetical zero depth. However, for tank aeration with gas depletion, Eq. (1) can be modified to:

$$\frac{dC}{dt} = K_L a_0(C^*_{\infty 0} - C) - gdp_{cw} \tag{8}$$

where $K_L a_0$ is as calculated by eq 2 to eq 6 inclusive from a known value of KLa, and a known value of the equilibrium saturation concentration C^*_{∞}, based on a $C^*_{\infty 0}$ is a parameter that would have existed without the gas depletion (note that $C^*_{\infty 0}$ is not C_S), and gdp_{cw} is the overall gas depletion rate during a clean water test. This equation is based on the Principle of Superposition in physics where the transfer rate is given by the vector sum of the transfer rate as if *gdp* (gas depletion rate) does not exist, and the actual gas depletion rate which is a negative quantity. $C^*_{\infty 0}$ cannot be the same as Cs because the latter is the oxygen solubility under the condition of 1 atmosphere pressure only, while $C^*_{\infty 0}$ should correspond to the saturation concentration of the bulk liquid under the bulk liquid equilibrium pressure, but minus the gas depletion (this of course cannot happen, since without gas depletion there can be no oxygen transfer). The hypothetical $C^*_{\infty 0}$ must therefore be greater than $C^*_{\infty 0}$ which in turn is greater than Cs since the former corresponds to a pressure of P_e (Figure 1) while the latter corresponds to P_a (say 1 atm). The hypothetical saturation concentration is not determinable, but this method of reasoning allows solving for the transfer from the baseline mass transfer coefficient as shown in eq 8. Since KLa is a function of gas depletion, and since every test tank may have different water depths and different environmental conditions, their gas depletion rates are not the same; hence, they cannot be compared without a baseline. Furthermore, by introducing the term gdp_{cw}, the oxygen transfer rate based on the fundamental gas transfer mechanism (the two-film theory) can be separated from the effects of gas depletions on K_La.

4. Theoretical Translation of Clean to Dirty Water Oxygen Transfer Rates

This gas depletion rate cannot be determined experimentally, since *gdp* varies with time throughout the test. Jiang and Stenstrom (2012) have demonstrated the varying nature of the exit gas (which is directly related to the *gdp* if the feed gas is constant) during a non-steady state clean water test. Therefore, the only equation that can be used to estimate the parameters is still eq. 1 as:

$$\frac{dC}{dt} = K_L a\,(C^*_{\infty} - C)$$

Eq. 1 is essentially equivalent to eq. 8 but expressed differently ($K_L a$ vs. $K_L a_0$). Therefore, by the same token, for in-process water without any microbes, eq 8 would become eq. 9 as follows:

$$\frac{dC}{dt} = K_L a_{0_f}\left(C^*_{\infty 0_f} - C\right) - gdp_{ww} \qquad (9)$$

Where the subscript *f* refers to the dirty water in the field, and subscript *ww* stands for wastewater or the reactor solution without the microbes, giving, in the presence of microbes based on the same mathematical principle of superposition, together with the principle of conservation of mass to include the microbial oxygen consumption rate *R*, the following:

$$\frac{dC}{dt} = K_L a_{0_f}\left(C^*_{\infty 0_f} - C\right) - gdp_{ww} - gdp_f - \mathrm{R} \quad (10)$$

where gdp_f is the gas side gas depletion due to the microbes only and R is the respiration rate, or when expressed differently as before:

$$\frac{dC}{dt} = K_L a_f\left(C^*_{\infty f} - C\right) - gdp_f - \mathrm{R} \qquad (11)$$

Note that in this equation, when $dC/dt = 0$, *gdpf* would be given by $K_L a_f$ ($C^*_{\infty f}$ - *C*) - *R*, where C becomes a constant, usually denoted by C_R. The inclusion of the phenomenon of gas-side oxygen depletion would lead to a modification of Eq. (2-2) and Eq. (2-3) in ASCE/EWRI 18-18 (ASCE 2018) and the derivation is given in the Appendix. Translation of clean to dirty water oxygen transfer rates is difficult because the variables affecting alpha α (the ratio of field $K_L a$ to clean water $K_L a$) are numerous and include aerator type, contaminants, level of mixing, etc. According to ASCE guidelines, measuring the oxygen uptake rate (OUR) under oxygen limiting conditions is extremely difficult, although the principle of respirometry is remarkably simple—-the slope of the decline curve of dissolved oxygen (DO) vs. time must be the respiration rate. The problem is not so much the method as the methodology commonly employed to make the sample measurable. When the oxygen level in the sample is low, say, at 2 mg/L, it would need to be artificially aerated to a higher level, say, 5 mg/L, before a meaningful curve (usually a straight line if the sample is not substrate-limiting as well) for calculating the slope can be obtained. This boosting of the DO concentration may make the sample measurement artificially high, and so the true uptake rate in the aeration tank is not measured correctly. [Another paper is being produced to address this artifact [18].

In the author's opinion, the method and procedures for translating CWT mass transfer coefficient $K_L a$ to dirty water mass transfer coefficient $K_L a_f$ should be included in all the standards for measuring oxygen transfer in clean water tests. It should be noted in passing that three mathematical principles are involved in the above derivations. They are, inter alia, the principle of mass conservation; the principle of mathematical induction; and, the principle of superposition of forces. They should not be confused by one another. For example, the respiration rate is based on mass balances, whereas, the gas depletion rate due to the microbes is based on superposition. The translation of the baseline mass transfer coefficient to the bulk mass transfer coefficient is based on mathematical induction, among other physical laws such as Dalton's Law, Henry's Law, the gas laws, Fick's Law, Le Chatelier's principle, and the two-film theory.

It should also be noted that the basic model as stated by eq. 1 is originally an empirical model based on much testing with clean water. The conventional model for in-process oxygen transfer is based on the principle of mass balance, but it is also an empirical model. Because they are empirical, their parameter estimation will depend on the circumstances and conditions in which the tests are conducted [19]. It is not possible to link two empirical models to expect a common evaluation of parameters, unless a link is found between the different models. The link is the microbial respiration rate which yields an exit gas depletion rate peculiar to a certain set of microbes. By superimposing this peculiar element to the clean water model, it becomes possible to link the two models theoretically and mathematically. Furthermore, the empirical model for clean water is proven mathematically from first principles, allowing formulating it to a theoretically based model for in-process water oxygen transfer as well, as given by eq. 11.

5. Measurement of Alpha Factor, α

Alpha is the ratio of the $K_L a$ of clean diffusers in process water to their $K_L a$ in clean water, and can range from approximately 0.1 to greater than 1.0 [note that this edition does not contain mentioning of Alpha]) [20-25]. It is influenced by a great number of process conditions, including surfactants, turbulence, power input per unit volume, geometry, scale, bubble size, sludge age, degree of treatment, and other wastewater characteristics. Ideally, the alpha factor would be measured by conducting full-scale oxygen transfer tests with clean water and wastewater, but this is normally impractical. Several studies have described small-scale [less than 50 gal (190 L)] oxygen transfer tests for measurement of the alpha factor, and a state-of-the-art method based on these studies has been suggested by Stenstrom and Gilbert (1981). In selection of an alpha factor for use in Equation (C1-1) [ASCE 2022], it should be borne in mind that, for a given wastewater stream, alpha is normally not constant, and a range of alpha values should be considered.

To circumvent the above uncertainty problem, the following procedure is recommended to be used in the bench-scale determination of the oxygen transfer coefficient, *α*:

A vessel similar to those shown in Figure 2 can be used. For the diffused system, where the gas-side gas depletion effect is significant and testable, an air measuring rotameter can be installed

for recording the gas flow rate. Clean water tests can then be performed with tap water as per ASCE 2022 until a reproducible K_La is obtained and re-aeration curves can be plotted, and the important parameters K_La and C^*_∞ can then be estimated using the non-linear least squares (NLLS) method as described in the standard.

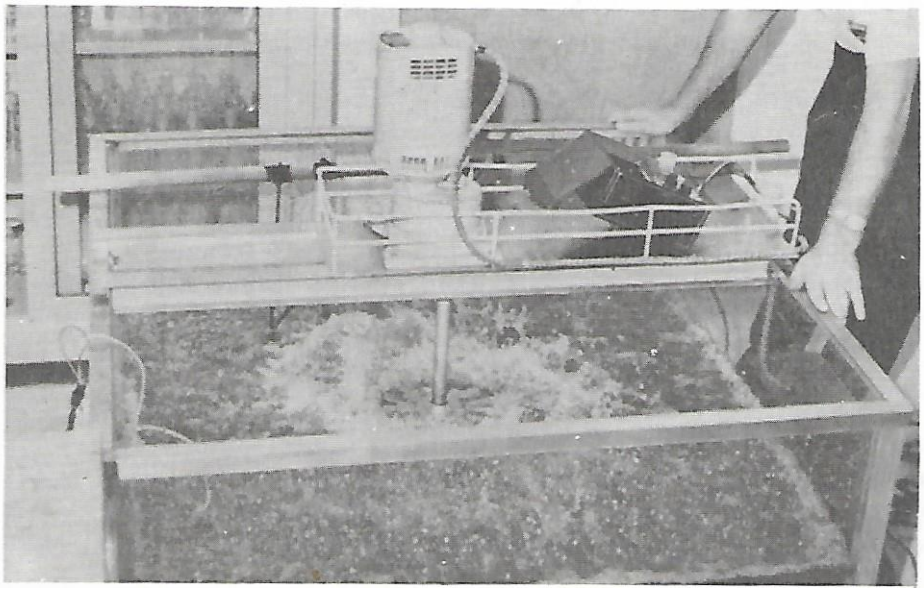

Figure 2: Laboratory apparatus for determination of α [26]

If wastewater is used in the test, the procedure should come after the clean water test, and should be repeated using the same volume of wastewater as the previous clean water test. As the test results would depend on the microbial respiration rate, as previously described, every effort should be made to eliminate the influence of the microbial respiration. This can be achieved by killing off all live microbes, such as using a sulphamic acid-copper sulphate solution, or if a bench scale biological reactor has been used, the effluent from the reactor should be used for the test when a completely mixed system is contemplated either in the entire aeration basin, or a section of the basin where completely-mixed is envisaged. If the latter method is used, the biological solids should be filtered out to prevent any microbial oxygen uptake that remains during the test period.

The respective K_La values as determined from the two tests (clean water vs. wastewater) can then be compared at the same temperature, pressure and mixing conditions, and α can be calculated in accordance with the following equation:

$$\alpha = (KLa\ wastewater)/(KLa\ clean\ water) \quad (12)$$

6. Measurement of Oxygen Uptake Rate (OUR) or the Respiration Rate R (ASCE 2018)

To estimate the in-situ respiration rate R, ASCE (2018) recommends the off-gas column steady-state test. In the recommendation, an acrylic or fiberglass reinforced tank is used, such as a 30 in. (760 mm) diameter by 11 ft (3.4 m) deep column. The column depth was selected based on work done at the University of Wisconsin where it was found that alpha decreased as the liquid depth increased over a range of two to ten feet (3.05 m); however, the decrease was relatively small above eight feet (2.4 m) [27]. Mixed liquor is continuously pumped to the test column from a position within the existing aeration tank using a submersible pump. The liquid detention time in the column is typically maintained between 10 and 15 min. The mixed liquor should be aerated using a fine pore (fine bubble) diffuser identical to the type used in the tank. The oxygen transfer efficiency of the diffuser used in the column using process mixed liquor is measured using the off-gas techniques described in Section 3.0 of the Guidelines. The airflow rate to the test diffuser is adjusted so that the DO concentration in the steady state column is maintained in the range of those found in the test section of the aeration basin. A schematic of the column test system is given in Figure D-1 of the ASCE Guidelines reproduced herewith as Figure 3 below.

Oxygen uptake rate is determined by a mass balance of oxygen around the column system as:
oxygen uptake rate = (oxygen transfer rate - net change in DO)/ column volume,
or,

$$R = (OTR_f - (DOo - DOi)\ Qi)/V \quad (13)$$

An example is given in the Guidelines as shown below:

An ex-situ column test is performed at a test section of the aeration basin. The following data are collected:
DOi (at transfer pump) = 0.55 mg/L where subscript i indicates inlet;
DOo (in test column) = 0.80 mg/L where subscript o indicates outlet;
qi (airflow rate to column) = 1.07 NL/s (normal litres per second)

OTE_f (measured in column) = 0.130 mg O_2 transferred / mg O_2 supplied

Qi (mixed liquor pump rate) = 2.16 L/s
V (column volume) = 1,460 L

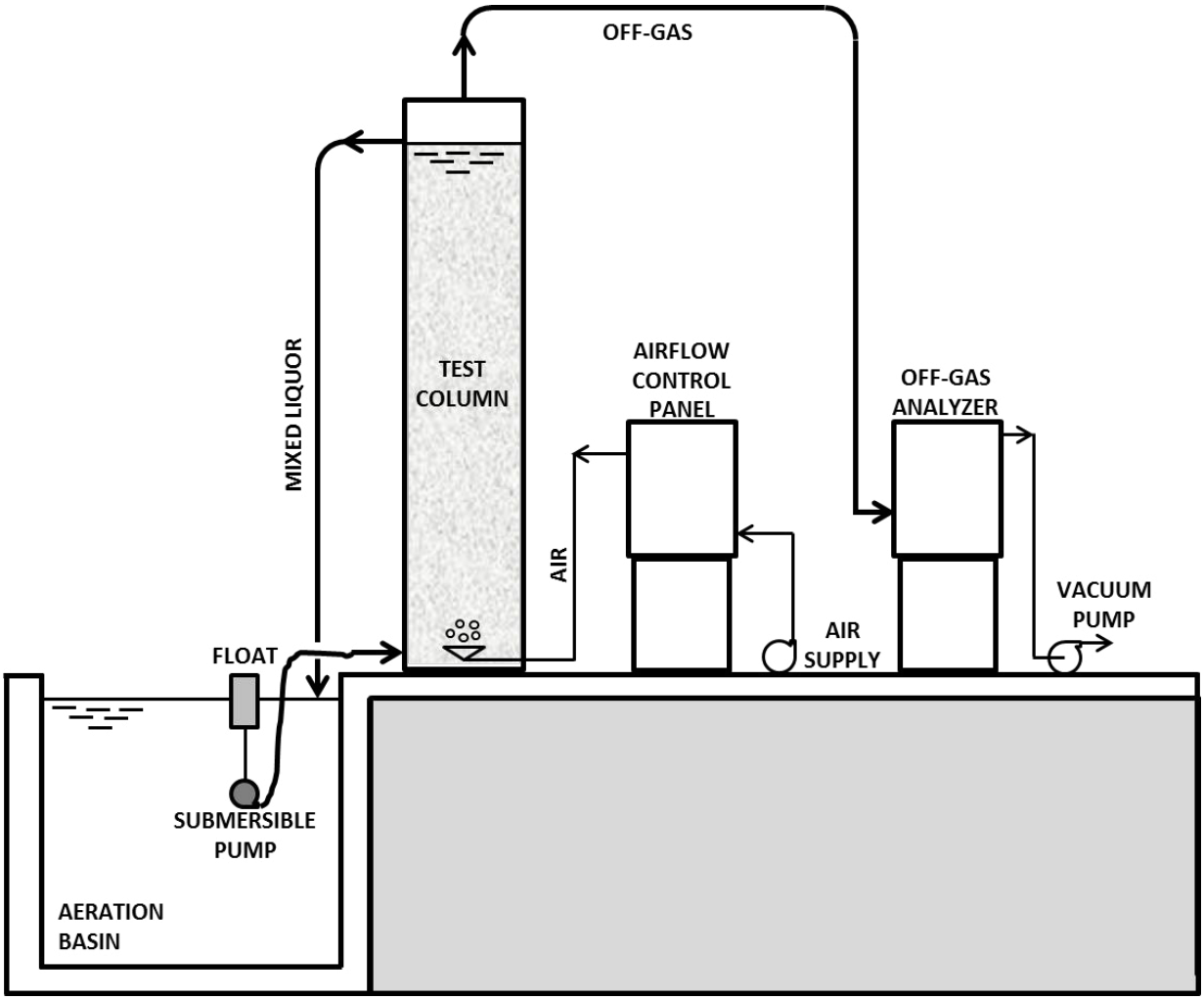

Figure 3: Mixed Liquor Steady State Column Test Schematic. [ASCE 2007] [ASCE 2018]

OTR_f = 1.07 NL air/s × 299.3 mg O_2/ NL air × 0.13 mg O_2 transferred / mg O2 supplied = 41.6 mg O2/s
R = [41.6- (0.80-0.55) × 2.16]/1,460 = 0.0278 mg/L•s × 3600 s/hr = 101 mg/L/hr

7. Measurement of Respiration Rate R (AWWA 2017)

Although, unfortunately, there is no comparable data by the other methods such as the BOD bottle method, Conducted a series of bench- and pilot-scale experiments to evaluate the ability of biochemical oxygen demand (BOD) bottle-based oxygen uptake rate (OUR) analyses to represent accurately in-situ OUR in complete mix-activated sludge systems [28]. Aeration basin off-gas analyses indicated that, depending on system operating conditions, BOD bottle-based analyses could either underestimate in-situ OUR rates by as much as 58% or overestimate in-situ rates by up to 285%. A continuous flow respirometer system was used to verify the off-gas analysis observations and assessed better the rate of change in OUR after mixed liquor samples were suddenly isolated from their normally continuous source of feed. OUR rates for sludge samples maintained in the completely mixed bench-scale respirometer decreased by as much as 42% in less than two minutes after feeding was stopped. Based on these results, BOD bottle-based OUR results should not be used in any complete mix-activated sludge process operational control strategy, process mass balance, or system evaluation procedure requiring absolute accuracy of OUR values. This echoes the author's suspicion about Eckenfelder's experiment calculating the oxygen transfer efficiency based on sample testing of the respiration rate which required artificial boosting of the DO concentration in a BOD-bottle, as described below.

There is certainly a need to get to the bottom of this. According to the published article, "Aeration Efficiency and Design", in which described two methods of testing for the microbial respiration rate, both the steady-state method and the non-steady state method were used to "validate" that these two methods are compatible

with each other. The results were given in a table as reproduced and summarized below (Table 1). In this table was shown the test results for 6 runs, for an aeration tank of 33 inches (838 mm) tall, and aerated at different flow rates from 33 cu ft/hr (0.016 m3/min) to 92 cu ft/hr (0.043 m3/min). In terms of SI units, the air flow rate (AFR) and the height-averaged air flow rate would essentially be the same given the small height. Eckenfelder used the log-deficit method to calculate the mass transfer coefficients, corresponding to each AFR, for the nonsteady state (NSS) test results, shown in red in col. 5. His data was reproduced and converted and then the non-linear regression analysis (NLLS) was used as recommended in the ASCE (2007) standard (2-06) or ASCE (2022) standard (2-22) to re-calculate the $K_L\ a$'s, shown in col. 4. The plot of the re-aeration curves is as shown in Figure 4.

These data were derived from an experimental aeration tank employing an agitator and air sparger ring. Next, the author used the steady-state (SS) method to again calculate $K_L\ a$, after using the measurements of the individual respiration rates from the BOD bottle method, and equating those with the oxygen transfer rate as $K_L\ a$ (C*-C), and the results are similar to those of the non-steady state method, ostensibly proving the validity of both test methods. Unfortunately, clean water tests were not performed, and so there is no way to estimate alpha α for these tests. However, the respiration tests were done at 2 mg/L as reported in the article by Eckenfelder, and so these samples must have been re-aerated by vigorous shaking to at least twice the value of the in-situ dissolved oxygen concentration.

If the author's hypothesis is correct, (i.e., that the microbial oxygen uptake rate is linearly proportional to the oxygen availability), then the measured R values must have been at least twice the actual values in the aeration basin where the samples were withdrawn. The resultant K_L a values would then be half the actual values measured by the non-steady state method. This experiment then in fact did not prove the validity of either one or the other, but instead proved that these two methods (NSS vs. SS) give results of $K_L\ a$ that are off by 50% using the ASCE methods.

Run No.	AFR	AFR	AVG. AFR	NSS	log-def	SS	rpt
	cu. ft/hr	m3/min	m3/min	calc. K_La 1/hr	rpt K_La 1/hr	K_La (ASCE) 1/hr	R (mg/L/hr)
	0	0	0	0	0	0	
C1	33	0.0156	0.0147	8.03	8.20	8.50	27.5
C2	39	0.0184	0.0173	11.31	9.80	9.37	30.5
C3	52	0.0245	0.0231	12.21	12.00	11.96	31.5
C4	64	0.0302	0.0284	16.01	15.00	15.89	34.4
C5	77	0.0363	0.0342	18.99	18.20	18.78	33.4
C6	92	0.0434	0.0409	24.87	23.50	22.70	32.2

Table 1: Experimental Test Result Using The Non-Steady State Test Method [Eckenfelder 1952]
Note: rpt = reported value; AFR = air flow rate; AVG.AFR = height averaged air flow rate

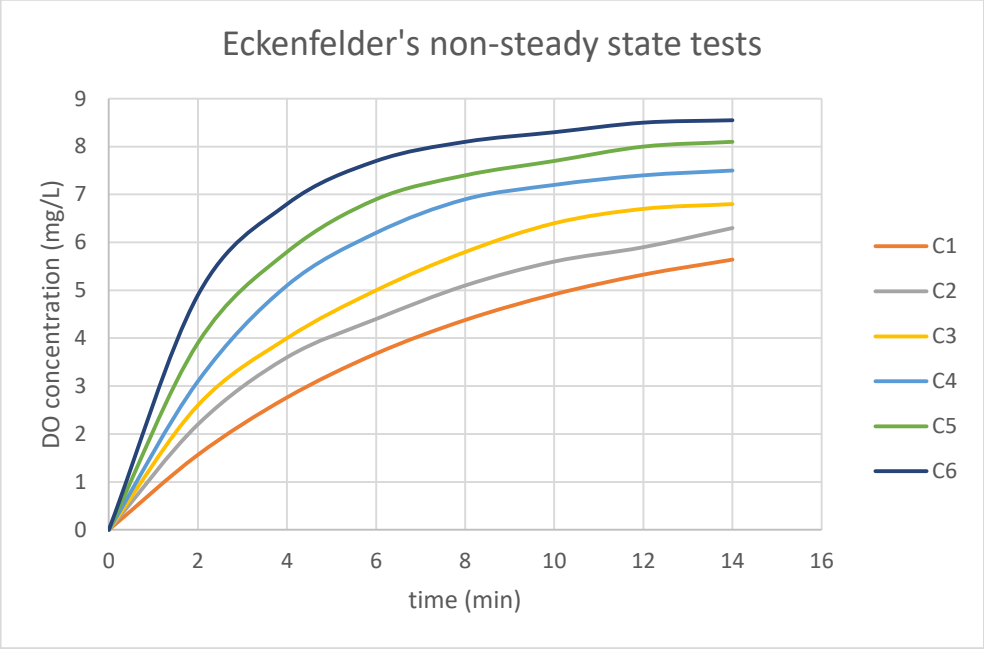

Figure 4: Illustrative problem in oxygen transfer measurement reproduced from Eckenfelder (1952)

According to the author's thesis, the equation for the steady-state method should come out to be $K_L\ a_f$ = 2R/ (C* -CR) instead of a single R as conventionally used, because of the gas depletion effect in the air bubbles. With this modification, this would then give the exact results of the K_L af as before using the ASCE non-steady state method, if it is reckoned that the BOD method of measuring the OUR is incorrect (over-estimation) because of the additional aeration. It is therefore vital, to prove one way or another, that an in-situ oxygen uptake rate test be performed similar to that described in the Guideline ASCE 18-96 (or more recently ASCE 18-18) for the steady-state column test using the off-gas measurement techniques. This may confirm, once and for all, whether oxygen availability has an effect on the oxygen uptake rate in a sample upon re-aeration.

The advantage of the off-gas method as shown in Figure 3, in measuring the respiration rate is that it does not require artificially aerating the sample to a higher DO level, and $K_L\ a$ does not come into the picture as well. The author would suggest that an experiment be done in one treatment plant with an acrylic column 3 m or so high; and then comparing the result with the traditional BOD bottle method and observing the difference, especially for oxygen-limiting low DO conditions. The key element of success is the off-gas analyzer that must measure the offgas accurately, since the OTE is highly sensitive to changes in the gas composition.

Measuring OUR under oxygen limiting conditions is difficult, and it was found that OUR measurements in general can be impacted by how the test is run. When one withdraws a sample of mixed liquor and runs an OUR test the typical way (aerate to high DO in a BOD bottle, stop aerating and then track the depletion of DO over time) one changes the conditions in the sample compared to the conditions in the aeration tank. Of course, that method is not at all appropriate for an aeration basin near zero DO (i.e., the tank OUR is limited by the oxygen transfer rate). When given more DO the bacteria will increase the OUR compared to the oxygen limited OUR in the aeration tank. But even with sufficient aeration basin DO, one can get different OUR values depending on the measurement method. For example, shaking the sample to aerate can break up the floc, making the substrate and DO more available to the bacteria. Doyle noticed in one of his theses that a BOD bottle-type OUR did not agree with a respirometer OUR. When using the old Arthur respirometer, it consistently gave higher OUR measurements compared to the BOD bottle/DO depletion method. He attributed it to the intensive aeration in the respirometer which was rather violent and may have broken up the floc causing increased delivery of DO and substrate to the floc. [Private communications Doyle and Lee].

8. Measurement of In-Situ Respiration Rate R (Non-Steady State Test)

In Garcia's experiment, there is a 50% reduction of the OUR when compared to the non-steady state test. An example using the In-process model (Eq. 11) is given in the supplemental material [29]. The dynamic measurement of the OUR and K_La is shown in Fig. S1. The calculation of CR is given in Table S2, using the Excel Solver method. Comparisons of the conventional model and the proposed model are illustrated by Eqs. (S1 to S4).

Garcia tried to explain this anomaly by the "cellular economy principle" that, during the time oxygen is not transferred, (i.e. during the shutting off the gas supply in the microbial desorption test), microbial cells consume oxygen at a lower rate. There are at least 4 reasons that this claim is wrong:

I. the desorption test is done in-situ, there is no time lag between DO (dissolved oxygen) analysis and sample collection;
II.The desorption curve is linear which means the decrease in DO content is uniform. This in turn means the microbes are consuming the oxygen at a uniform rate. If the microbes had been using oxygen at a declining rate, the curve would have been concave in shape;
III. During desorption, there is still plenty of oxygen in the liquid phase, beginning at 55% saturation which is quite high. Bacteria are not so smart that they could sense a continual diminishing of oxygen that they would start economizing from the start. Only when the DO has reached the endogenous zone would this occur. Even if the consumption rate has decreased it could never by as much as 50%.
IV. There is no deficiency in soluble substrate and so the respiration rate would not be affected by soluble substrate uptake depletion, i.e. the system was not at substrate-limiting condition before or during the test.

According to Doyle, there is no data to show that is not the case that the microbes change their respiration rate at low DO levels, but it seems that oxygen is used as fast as it can be delivered under low DO conditions. Any reduction in oxygen uptake rate is due to physical/chemical limitations (diffusion limitations, and concentration gradients and transport across the cell membrane). It would be difficult to determine whether the microbes are doing this voluntarily since to test the theory one has to limit the DO, which impacts the other factors mentioned, such as an increase in the biological floc respiration rate due to the breaking up of the floc by violent agitation in order to bring the DO level back up to a measurable level for testing.

In summary, the author reckons there are only three possible explanations for the increase of the OUR. Firstly, when the sample is agitated by vigorous shaking, the activity level of the microbes might increase. Like athletes they respire more. Secondly, the oxygen level in the sample may be limiting (although at 2 mg/L, it shouldn't be); thirdly, suggested a cell economy principle by which the microbes voluntarily reduce the respiration level at low DO and changes the respiration rate at elevated level due to increased oxygen availability. There have been many literatures on this but none seems to have given a definite answer.

In the article by Doyle (1981), it was suggested an interesting method of testing for alpha. It appears that it may be possible to use the dilution method as suggested by the article to test out the determination. By first aerating a tank of pure water to an elevated DO, say to 7 mg/L, and then gradually pouring a sample of the activated sludge mixed liquor into the tank, and then gently mixing them together, it may be possible to measure the slope of the DO decline curve at quiescent conditions, thereby eliminating the first possible explanation for the cause of increased OUR measurement. If the sample has been diluted to 50% by the tank, the resultant slope should then be multiplied by 2 to get the true OUR. This should then be compared with the steady-state column test with an in-situ measurement as recommended by the ASCE Guidelines.

9. Practical Translation to In-Process Oxygen Transfer

In the application for wastewater treatment, using the transfer of oxygen to clean water as the datum, it may then be possible to determine the equivalent bench-scale oxygen transfer coefficient (K_La_{f0}) for a wastewater system, and the ratio of the two coefficients can then be used as a correction factor to be applied to fluidized systems treating wastewaters via aerobic biological oxidation, where microbial respiration has a significantly different contribution to gas depletion compared to clean water. However, before any mass balance equations can be used to evaluate this difference in the gas depletion rates, it is paramount to determine alpha (α) where alpha is the correction factor (Rosso D. and Stenstrom, M. 2006) given by:

$$\alpha = \frac{K_L a_{f_0}}{K_L a_0} \approx \frac{K_L a_f}{K_L a} \qquad (14)$$

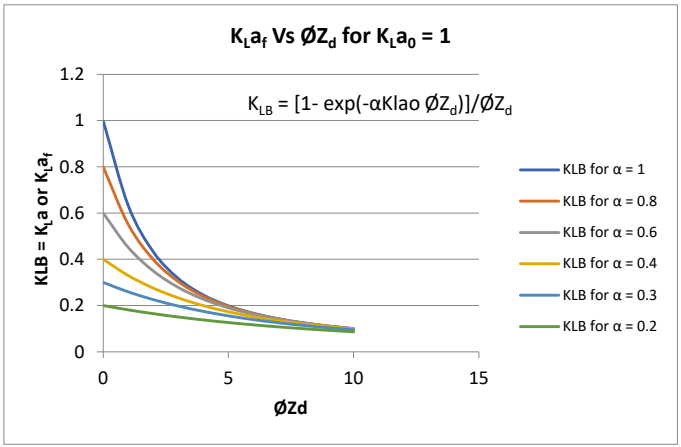

Figure 5: The apparent K_La_f plotted against $ØZ_d$ for $K_La_0 = 1$

(where $K_{LB} = K_La$ for water (α = 1) or K_La_f for wastewater (α < 1)) It is postulated that this correction factor (α) can be determined by bench scale experiments or by pilot tests. It is hypothesized that this alpha value is not dependent on the liquid depth and geometry of the aeration basin and the model developed that relates K_La to depth then allows the alpha value to be used for any other depths and geometry of the aeration basin where the mass transfer coefficient can be generically represented by a function K_{LB}.

Therefore, using Eq. (2), after incorporating ***α*** into the mass transfer coefficient for in-process water, the mass transfer coefficient in in-process water K_La_f would be given by K_{LB}, i.e.,

$$K_La_f = \frac{1 - \exp(-\Phi Z_d . \boldsymbol{\alpha} K_L a_0)}{\Phi Z_d} \qquad (15)$$

This equation can be plotted for K_La_f against the function $ØZ_d$ for when the baseline is unity, for various α values, as shown in Figure 5 above. This equation Eq. 2, requires that Ø is given by $Ø = x(1\text{-}e)$ where x is as defined previously for eq. 2 to eq. 6.

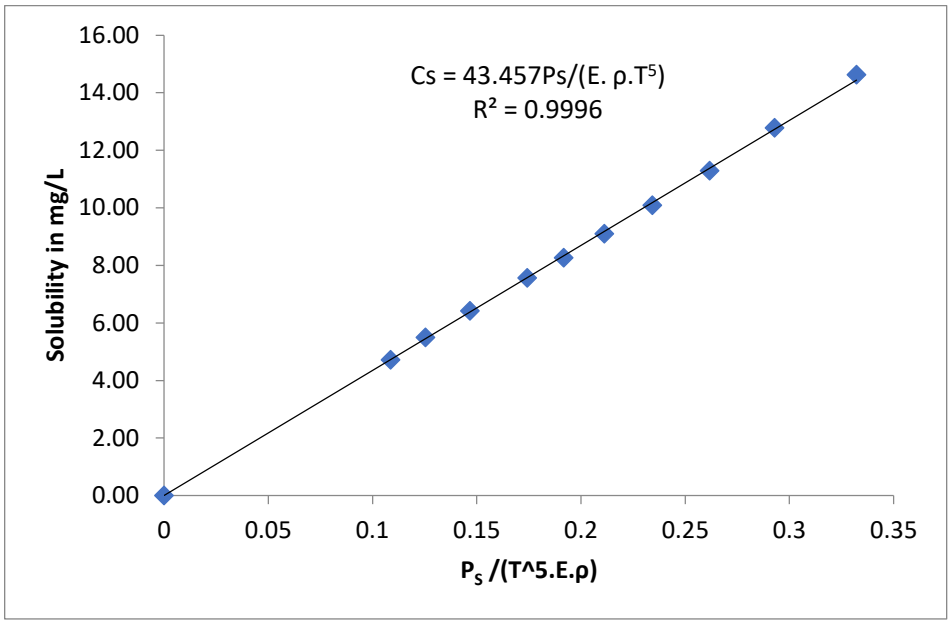

Figure 6: Solubility Plot for water dissolving oxygen at Ps = 1 atm (1.013 bar)

If the handbook data of oxygen solubility is plotted against the inverse of the temperature correction function affecting solubility, the straight-line linear plot would be as shown in Figure 6 below. Therefore, the solubility law [Lee 2017] can be expressed either by the equation derived from plotting the insolubility, or expressed by the equation from plotting the data as in Figure 6. In the former method, the equation gives the insolubility of oxygen expressed by:

$$\frac{1}{Cs} = 0.02302.T^5 \times E \times \frac{\rho}{Ps} \qquad (16)$$

where T is in K(Kelvin) to the power 10^{-3}.

In the latter case, the equation gives the solubility directly and is expressed by:

$$Cs = 43.457 \times \frac{Ps}{(T^5 E\rho)} \qquad (17)\#$$

Henry's Law is applicable only to ideal solutions and for an imperfect liquid subject to changes in physical state, at extreme temperatures between 273 K and 373 K, it is only approximate and limited to gases of slight solubility in a dilute aqueous solution with any other dissolved solute concentrations not more than 1 percent [30]. Since in Henry's Law, the solubility Cs is proportional to pressure, the Henry's Law constant would be given by H = 43.457/ (T^5 Eρ). In a mixed liquor, the liquid density may depart from that of clean water significantly, and so the sample should be measured for its density using a hygrometer to measure the humidity and a hydrometer to measure the relative density.

The use of this equation as well as eq. 15 for in-process water parameter estimations will be the subject of additional research, not so much on validating the model as to find its limitations and boundary conditions. The graph of Figure 5 shows exactly what Boon (1979) has found in his experiments, that KLaf is a declining trend with respect to increasing depth of the immersion vehicle of gas supply. Once KLaf is determined, eq. 11 can be used to determine the OTRf in the actual aeration tank or section of the aeration tank in a complete-mixed system.

10. Conclusions

1. In this manuscript, the author postulates that the true OTR_f is given by $K_L a_f$. (C^*_f - C) - R, since the transfer rate is affected by biochemical reactions in the cells, which changes not only the water characteristics but also changes the gdp.

Based on the studies so far cited in this manuscript, it is concluded that the standards should be amended as follows [31].

2. The oxygen transfer efficiency based on the oxygen transfer rate by a prescribed CWT (Clean Water Test) for a fixed gas supply is a property of an aeration equipment, and so will not be affected by external factors (i.e. clean water test data are reproducible) [ASCE 2007] and would be uniquely defined by a standard specific baseline value $K_L a_0$ [Lee 2018];

3. A new mathematical model for *gdp* has been derived (Eq. 2 to eq. 6) and is verified by testing under a variety of water depths for clean water (Lee 2018). This model is shown to be applied to wastewater through an alpha (α) that pertains specifically to wastewater characteristics (see Eq. 15) [32,33].

4. The respiration rate produces additional resistance to oxygen transfer in the system resulting in a loss of *gdp*, that would lead to an increase in the exit gas oxygen content compared to the CWT at the process DO level, and therefore must be accounted for in the mass balancing equations. In this sense, the OTR_f in the system (as

opposed to the aeration efficiency of the device definable by the CWT) is affected negatively by the OUR;
5. The difference in the gas depletion rates due to the microbial cells that affect oxygen transfer is deemed to be precisely the respiration rate itself (see Figure 1), based on all the test results, and therefore is important for the revising of the ASCE equation [34,35].
6. The present equations used in the ASCE Guidelines [1997] are not correct for submerged aeration. This has resulted in discrepancies of around 40 ~ 50% in the estimation of KLaf for batch test analyses (i.e. the steady-state test results are lower than the non-steady state tests by such). The new equations after incorporating the effect of gdp, give an overall much less discrepancy notwithstanding the various inaccuracies of the individual methods stated in the literature [ASCE 1997] and for the continuous water flow testing;
7. $K_L a_f$ is dependent on the AFR (air flow rate), but since the AFR also affects the corresponding KLa in clean waters, the resultant effect on α is not overly significant. The average value of α based on all the test results is about 0.82 for domestic sewage, according to Mahendraker's data. This value of α is in line with the traditional design value of 0.8 used in many treatment plants' designs. However, using this value would now require revising the design equations to include the gas depletion effect as explained in this manuscript, otherwise, α would become highly variable [36-38].

As a consequence of including the gas depletion effect in the application of clean water test results to estimate oxygen transfer rates in process water at process DO levels, for the same oxygenation system, the oxygen transfer equation should be given by eq. 11 which translates into the following amendment, applicable to Eq. CG-1 in ASCE 2-06 [ASCE 2007]:

$$OTR_f = \left(\frac{1}{(C^*_\infty)_{20}}\right)[\alpha\,(SOTR)\Theta^{T-20}]\left(\tau.ß.\Omega.(C^*_\infty)_{20} - C\right) - 0.001RV \qquad (18)$$

With all symbols and units referring to the ASCE (2007) Standard. In this equation, α is calculated by eq. 14 and as determined by the method described in section 5. The implication of eq. 18 is that the oxygen transfer in the field of an aeration equipment can be closely determined by clean water tests by applying relevant correction factors to the clean water measured parameters, together with accurate measurements of the respiration rate in the field. To complete the equation, the effects of temperature in the selection of a proper value for the temperature correction parameter Θ, and the effect on KLa due to geometry have been discussed in previous manuscripts.

The current use of a single constant value to represent the α-factor as used in the standards has a tremendous flaw as is recognized [39]. Their proposed solution is to change the current practice of a constant alpha (α) to using a dynamic α-factor, and to use a dynamic model to describe aeration energy demand, both in 24-hour periods with organic load variations and α-factor changes. It would be interesting to compare their results, when such a dynamic model becomes available, to the results based on eq. 15, eq. 16 (or eq. 17) and eq. 18, using the approach recommended in this manuscript which is to separate the dual effects of respiration rate and wastewater characteristics, when more data with regard to both approaches are gathered.

Other concerns that may affect the ultimate purpose of translating clean water tests to process water involve principally in how the clean water oxygen transfer testing can be made more accurate, and the concerns are categorized as: 1) securing accuracy by using incomplete-mix models; 2) securing accuracy by using loop model; 3) quantifying uncertainty for standard test; 4) including probe characteristics in data analysis; 5) replacing the sulphite method and exploring the temperature effect that may affect the accuracy of the method; 6) securing accuracy by not applying standard values (e.g. the submergence depth ratio de/Zd); and, 7) performing uncertainty budget to understand the reliability of test results. The author would add that, since has stipulated that the mixing from the atmosphere may have an effect on KLa, this effect should be quantified in a CWT [40]. These, and other concerns, such as the effect of metabolic heat generation, will be subject to further research. For this paper, it is assumed that an adiabatic process which is a type of thermodynamic process that occurs without transferring heat or mass between the thermodynamic system and its environment, prevails. For discussion about uncertainty involved in the data collections and other related aspects, the author is of the opinion that the present standards already cover these topics well [41-43].

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