

Article Title: Development of The Oxygen Mass Balance Equation for aerobic bioreactors

Date: Sep 15, 2020

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Abstract

Current application of clean water aeration test standards for wastewater treatment systems is based on the most commonly used standards for the clean water test. All the standards are mostly unified in respect to the methodology employed to calculate the oxygen mass transfer coefficient K_La , but the standards fall short of how to extrapolate the test result to field conditions. This paper addresses a problem common to all the standards, which is the application of clean water test result to Process Oxygen Transfer Rates. By modifying the conventional model used by the standards for this application, and if proper OUR (oxygen uptake rate) methods can accurately determine the respiration rate, this paper attempts to show that the clean water tests can be used to determine the oxygen transfer efficiency of an aeration device in the field. The new model is based on previously developed mathematical models, and also based on the novel concept of a resistance to gas transfer due to microbial activity in the field. As previous published papers by the author have demonstrated the veracity of scaling up of the mass transfer coefficient for clean water, so a logical extension of the modelling effort to include scale-up for wastewater is presented in this paper, to allow for varying gas rates, submergences, and microbial activity, considering the influence of exit gas depletion due to such effects. It is postulated that the relative mass transfer coefficient, α (alpha), the ratio of mass transfer coefficient in wastewater K_{La_f} to mass transfer coefficient in water K_{La} , is independent of microbial activities in an aeration basin and the corresponding performance ratio in terms of efficiencies is also the same function as $\alpha = OTE_f/OTE$, where the subscript f stands for field water characteristics. It is postulated that this α is not the same as the ratio OTE_{pw}/OTE that gives only a false alpha, where the subscript pw stands for process water undergoing biological stabilization due to microbial metabolism. The field-determined OTE_{pw} is affected by the respiration rate R that is dictated by the microbial activity, which is mathematically associative to the transfer process by addition (based on the superposition principle), and not associative by multiplication with a scalar quantity. A gas-phase mass balance for oxygen around a completely mixed aeration tank confirms the association nature of the alpha-factor. This is the most important distinction between OTE_{pw} and OTE_f in any attempt to translate clean water test results to wastewater oxygen transfer. Examination of test data extracted from the literature indicates that this is indeed the case.

1. Introduction

(Note: Unless otherwise stated, this paper pertains to all the nomenclature as defined in ASCE 18-18)

It is universally acknowledged that, under the steady-state process conditions, when the dissolved oxygen (DO) concentration in an aerobic reactor is constant, the oxygen uptake rate (OUR), also denoted as R for the microbes' respiration rate, is equal to the oxygen transfer rate (OTR) assuming no other oxygen-consuming reaction is simultaneously occurring. In general, before a steady state is reached, this understanding leads to the following liquid-phase mass balance equation for oxygen around a completely mixed aeration tank:

$$\frac{dC}{dt} = K_L a_f (C_{\infty f} - C) - R \quad (1)$$

where the subscript f stands for field conditions, and $K_L a_f$ can be expressed as $\alpha \cdot K_L a$, where α the relative mass transfer coefficient, is the ratio of mass transfer coefficient in wastewater $K_L a_f$ to mass transfer coefficient in water $K_L a$. The above equation applies to a batch reactor only, without liquid inflow or outflow. Unfortunately, this universal equation is, in fact, theoretically misleading because it is more than just a mass balance equation. It also includes an energy balance as it is derived from an energy balance for gas transfer based on the two-film theory [Lewis and Whitman 1924] and the concept of a driving force. The implicit energy balance in this equation is not correct. This paper aims to amend this equation from first principles in order to put forward a more realistic model for practical use.

In submerged aeration of a wastewater treatment plant, when a steady state is reached (i.e., the oxygen supply meeting the oxygen demand from the biological system), the mole fraction of oxygen in the gas phase would decrease progressively as the depth decreases, so that the exit gas has a smaller mole fraction than the feed gas. The exit gas depletion (the difference between the

feed gas and the exit gas is termed the exit gas depletion) becomes important when the aeration tank is not shallow [Lee 2018]. There is evidence that the gas depletion rate (*gdp*) or the oxygen transfer rate is affected by any biochemical reactions such as the respiration rate of any microorganisms occurring within the liquid. This effect of changes in the gas depletion rate with respect to changes in the mixed liquor suspended solids (MLSS) under a constant gas flow rate is illustrated by Hu J. (2006) as shown in Fig. 5 and Fig. 6. The hypothesis presented in this manuscript is that, for the same gas supply rate, the effect of such reactions is a negative impact on gas depletion, so that the higher the reaction rate, the smaller is the gas depletion rate, and therefore less gas will be transported or transferred into the liquid under aeration. In mathematical terms, $F_1 - F_2 = R$, where F_1 is the gas depletion rate unaffected by any biochemical reactions; F_2 is the gas depletion rate in the presence of biochemical reactions in the liquid, and R is the reaction rate or the microbial respiration rate or the microbial oxygen uptake rate (steady-state OUR_f) where the subscript *f* refers to field conditions.

2. Theory

In the energy balance, the driving force comes from the concentration gradient, similar to the driving force for a flowing pipe that comes from the hydraulic gradient between the source and the sink. If the pipework is entirely frictionless, then the potential energy (P.E.) prior to opening the tap is entirely converted to kinetic energy (K.E.) when it is discharged to the sink without any energy loss in between. When the pipework is not frictionless, there will be some energy loss due to the resistance to flow arising from the pipe friction, and so, in mathematical terms:

$$P.E. = K.E. (at exit) + loss(2)$$

or

86
$$P.E. = K.E. (frictionless) - loss(3)$$

87 Note that this friction loss only occurs when there is flow. The resistance is gone as soon as the
88 tap is closed.

89 Certainly, energy is expended when transferring mass of fluid from the source to the sink. This is
90 the same with gas transfer. For a fixed energy input, this energy expenditure can be estimated by
91 energy balance.

92 Campbell (2020) postulated that, for Oxygen Transport and Uptake in an Activated Sludge
93 Reactor, for the Gas-Liquid-Solid Model, the movement of oxygen from the bulk gas phase to
94 the microbes located within the solid phase involves several discrete steps. First oxygen must
95 move from the bulk gas (Step 1) through the stagnant gas boundary layer (Step 2) across the gas-
96 liquid interface. The oxygen is then transferred across the stagnant liquid boundary layer (Step 3)
97 into the bulk liquid (Step 4) and across the stagnant liquid boundary layer (Step 5) to the
98 biological floc surface.

99 The oxygen must cross the liquid-solid interface and diffuse through the porous EPS
100 (extracellular polymeric substance) layer present within the microbial floc (Step 6). Once the
101 oxygen reaches a microbial cell, the oxygen can be transported across the cell membrane where
102 the oxygen is utilized by the cell internally for respiration (Step 7).

103 In this process, work is done when oxygen is transferred from the bulk gas in the bubble to the
104 liquid solid interface, having to overcome several hurdles as energy is expended over each. The
105 denser is the microbial floc, the higher would be the resistance build-up, and the more difficult
106 the gas gets transferred to the liquid phase. Therefore, the oxygen transfer rate is not just given
107 by the two-film theory in clean water where the oxygen transfer rate (OTR) is given by:

$$\frac{dC}{dt} = K_L a (C_{\infty}^i - C) \quad (4)$$

but would be given by (as similar to eq. 3 for the hydraulic analogy):

$$OTR = \frac{dC}{dt} - R \quad (5)$$

or

$$OTR = K_L a (C_{\infty}^i - C) - R \quad (6)$$

where the terminologies such as the mass transfer coefficient and the saturation concentration are understood to refer to those equivalent parameters pertaining to the contaminated liquid instead of clean water. In this instance, R is the resistance to transfer because of the insertion of the microbes that establishes an oxygen molecular pathway for transferring the dissolved gas to the microbes. The microbes are the sink which, in the analogy of the hydraulic pipework flow, will not exist if the microbes' biological activities are turned off. The pathway is immediately established upon the resumption of these microbial functions. The above equation represents the energy balance during the oxygen flow process, based on the principle of superposition of forces. This energy balance is to be distinguished from the mass balance of oxygen in the system, where the accumulation rate of the oxygen in the bulk is the difference between the rate of transfer, and the rate of metabolic utilization by the microbial cells. Hence,

$$\frac{dC}{dt} = OTR - R \quad (7)$$

Therefore, substituting eq. 6 into eq. 7, we have

$$\frac{dC}{dt} = K_L a (C_{\infty}^i - C) - R - R \quad (8)$$

The above equation can be theoretically developed by conducting a gas-phase mass balance for oxygen around a completely mixed aeration tank for the case of a simple batch process.

3. Mathematical Development based on Gas-phase Mass Balance

(i) Baseline ($R = 0$)

First consider the baseline case (reactor solution). For the simple case where oxygen uptake rate is zero, ASCE 18-18 (Eq. 2-2) [ASCE 2018] based on a mass balance on the liquid phase gives:

$$\frac{dC}{dt} = K_L a_f (C_{\infty f}^i - C) \quad (9)$$

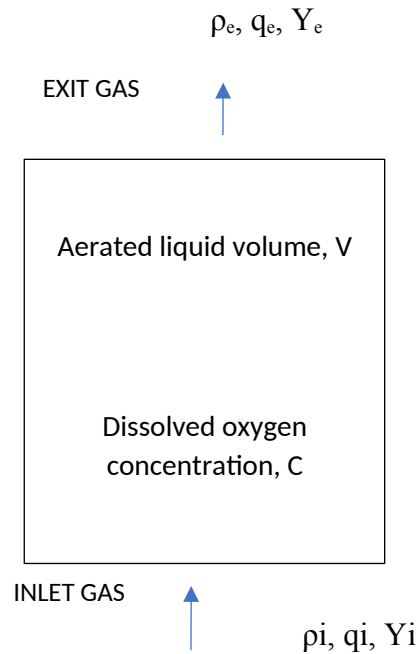


Fig. 1. Mass Balance on the gas phase

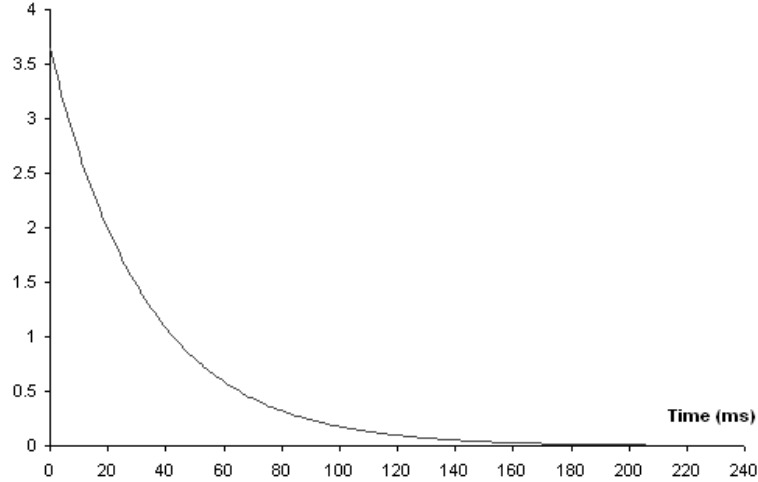
Based on a mass balance on the gas phase (oxygen depleted in gas equals the oxygen absorbed by liquid) gives:

$$F = K_L a_f (C_{\infty f}^i - C) \quad (10)$$

where F is the gas-side gas depletion rate per unit volume given by Figure 1, and so,

$$F \cdot V = \rho_i q_i Y_i - \rho_e q_e Y_e \quad (11)$$

152 where ρ is density of the gas; q is the gas flow rate; Y is the oxygen mole fraction; subscripts i
 153 and e refer to inlet and exit respectively.



154
 155 Figure 2. Gas Depletion Time Variation ($R = 0$)

156 Simplifying the case by assuming the test starts at zero DO, and

157 integrating Eq. (9) gives:

158
$$C = C_{\infty f} \left(1 - \exp(-K_L a_f \cdot t) \right) \quad (12)$$

159 Substituting C from the above expression into Eq. (9) gives:

160
$$\frac{dC}{dt} = K_L a_f \left(C_{\infty f} - C_{\infty f} \left(1 - \exp(-K_L a_f \cdot t) \right) \right) \quad (13)$$

161 Hence,

162

163
$$\frac{dC}{dt} = K_L a_f \cdot C_{\infty f} \cdot \exp(-K_L a_f \cdot t) \quad (14)$$

164 The oxygen depleted in gas and the oxygen absorbed by liquid are the two sides of the same

165 coin, and so, since Eq. (9) and Eq. (10) are identical, ($dC/dt = F$), therefore,

166
$$F = K_L a_f \cdot C_{\infty f} \cdot \exp(-K_L a_f \cdot t) \quad (15)$$
 Therefore,

167 $F(t=0) = K_L a_f \cdot C_{\infty f}^i$ (16)

168 and, $F(t=\infty) = 0$

169 Plotting this function F for gas depletion would give an exponential curve as shown in Figure 2.
 170 This is the baseline case plot. Without the action of microbial respiration, the oxygenation
 171 capacity of the aeration system is fully utilized. Eventually, the system will balance itself so that
 172 the tank becomes saturated, and the gas transfer is complete. Further continual supply of gas
 173 would not increase the oxygen content in the tank, and the system is said to be in a steady state,
 174 as the feed gas is balanced by the exit gas, and there is no gas depletion at steady state.

175 (ii) ASCE model for $R > 0$

176 In the presence of cell respiration, according to current ASCE 18-18, Eq. (3-1), the gas depletion
 177 rate remains the same under the influence of R, but ASCE Eq. (2-2) now becomes:

178 $\frac{dC}{dt} = K_L a_f (C_{\infty f}^i - C) - R$ (17)

179 Integrating Eq. (17) with respect to time, gives

180 $\frac{K_L a_f \cdot (C_{\infty f}^i - C) - R}{K_L a_f (C_{\infty f}^i - C_0) - R} = \exp(-K_L a_f \cdot t)$ (18)

181 Again, assuming $C_0 = 0$, at time $t = 0$, and re-arranging terms,

182 $C = C_R \left(1 - \exp(-K_L a_f \cdot t) \right)$ (19)

183 where

184 From eq. (17), $dC/dt = 0$ at steady-state, and $C = C_R$, then

185 $C_R = C_{\infty f}^i - \frac{R}{K_L a_f}$ (20)

186 Substituting Eq. (19) into Eq. (17) for C, we have

187 $\frac{dC}{dt} = K_L a_f \left(C_{\infty f}^i - C_R \left(1 - \exp(-K_L a_f \cdot t) \right) \right) - R$ (21)

188 Simplifying,

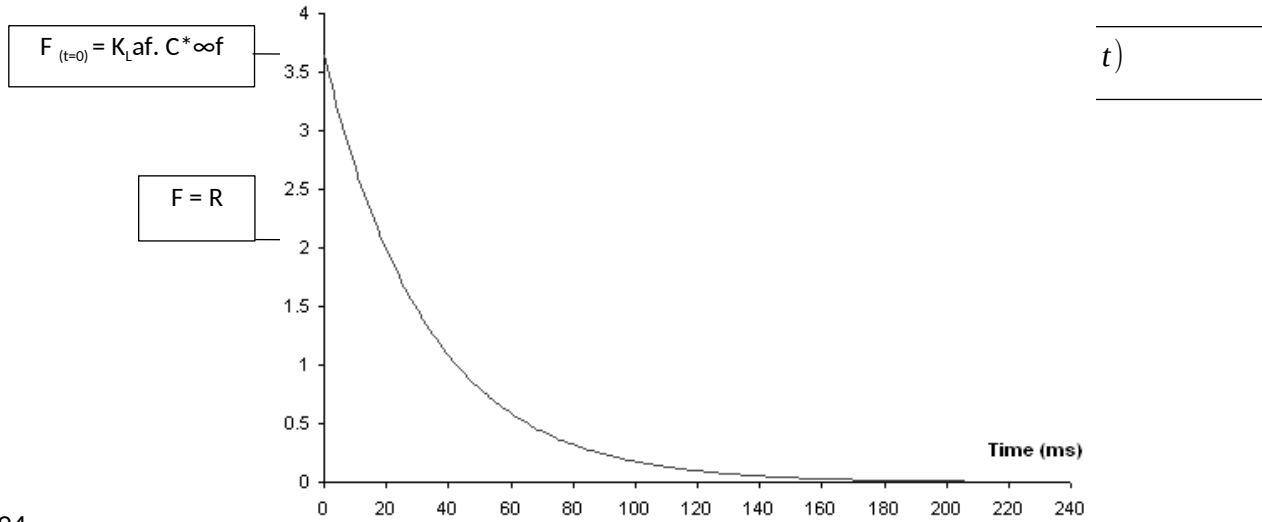
189 $\frac{dC}{dt} = K_L a_f \cdot C_R \cdot \exp(-K_L a_f \cdot t) \quad (22)$

190 From ASCE Eq. (3-1), where ASCE has assumed to be same as the baseline case,

191 $F = K_L a_f (C_{\infty}^i - C) \quad (23)$

192 Differentiating w.r.t. t ,

193 $\frac{dF}{dt} = -K_L a_f \cdot \frac{dC}{dt} \quad (24)$



194

195 Fig. 3. Gas Depletion Time Variation ($R > 0$) [ASCE model]

196 Substituting (22) into (24),

197 $\frac{dF}{dt} = -K_L a_f \cdot K_L a_f \cdot C_R \cdot \exp(-K_L a_f \cdot t) \quad (25)$

198 Integrating,

199 $F = K_L a_f \cdot C_R \cdot \exp(-K_L a_f \cdot t) + K \quad (26)$

200 where K is an integration constant.

201 The boundary condition is that when $t \rightarrow \infty$, $F \rightarrow R$, and therefore $K = R$

202 Hence,

203 $F = R + K_L a_f \cdot C_R \exp(-K_L a_f \cdot t) \quad (27)$

204 but since from eq. 20,

205 $C_R = C_{\infty f}^i - \frac{R}{K_L a_f}$

206 Therefore,

207 $F = R + (K_L a_f \cdot C_{\infty f}^i - R) \exp(-K_L a_f \cdot t) \quad (28)$

208 at $t = 0$, therefore,

209 $F = K_L a_f \cdot C_{\infty f}^i$

210 Therefore, at $t = \infty$, $F = R$, the plot obtained is as shown in Fig. 3.

211 The plot is similar to the baseline plot, except that the final steady state gas depletion rate at
 212 infinite time is not zero, but is given by the fixed respiration rate R . At steady state, therefore, the
 213 respiration rate equals the gas depletion rate which is concurrent with the thesis of this paper.
 214 However, this plot in Figure 3 shows that the gas depletion is not impaired at the beginning in
 215 the presence of R . Like the previous plot for the case where cells are absent, the oxygenation
 216 capacity is fully utilized at time $t = 0$. Experiments have shown that this is not the case, and it is
 217 really not logical, since R must affect the gas depletion rate, no matter whether it is at the
 218 beginning, during, or at the end of the test. Mancy and Barlage (1968) described the phenomenon
 219 where long chain charged molecules attach to the gas bubble interfaces and impede the diffusion
 220 of oxygen to bulk solution. The longer the bubbles are in transit to the surface the more of these
 221 materials are attached to the bubbles resulting in a greater resistance to oxygen transfer and a
 222 reduction in alpha (α) which is the relative mass transfer coefficient (K_{La}) of in-process water
 223 compared to clean water. Rosso and Stenstrom (2006) have found that bubble surface
 224 contamination equilibrates even before detachment, so that after bubble detachment and during
 225 the transit of bubbles through the liquid, the liquid-side gas transfer coefficient K_L is reduced to a
 226 steady-state process value, *always lower than the gas transfer coefficient in pure water*. This
 227 means that the gas depletion must occur almost immediately upon detachment, and if the cells

228 exert a transfer resistance, then the *reduction* of the gas-side depletion rate must start upon
 229 detachment at time $t = 0$, neglecting the bubble formation stage which is small compared to the
 230 time taken for the bubble transit to the surface. Therefore, the *gdp* (gas depletion rate) F at $t = 0$
 231 must be smaller than the baseline case at $t = 0$. They should not be the same. This graph based on
 232 the ASCE model must therefore be incorrect.

233 (iii) Proposed Model for $R > 0$

234 Going through the same process, but with the ASCE Eq. (2-2) proposed to be changed to:

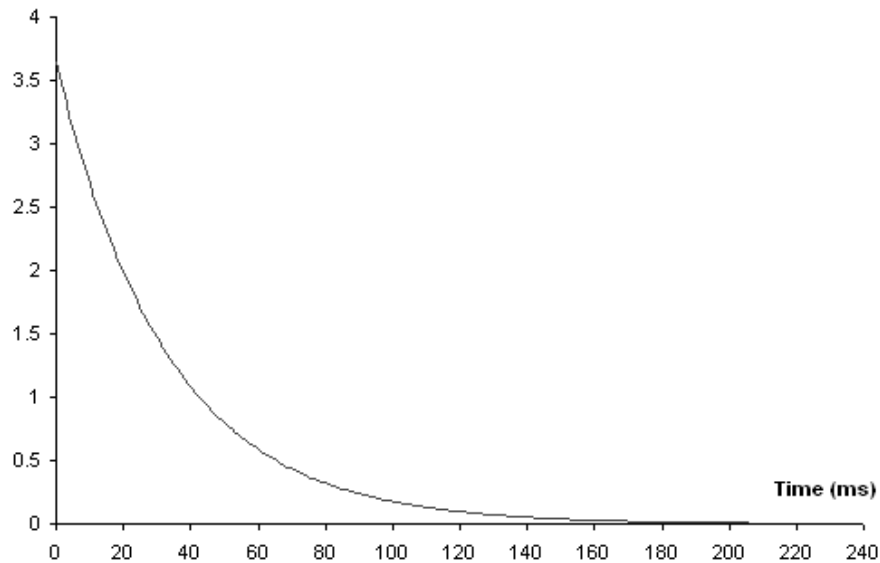
235
$$\frac{dC}{dt} = K_L a_f (C_{\infty f} - C) - 2R \quad (29)$$

236 and the gas phase mass balanced is changed to:

237
$$F = K_L a_f (C_{\infty f} - C) - R \quad (30)$$

238 the same expression for the gas depletion function is obtained, i.e.,

239
$$F = R + K_L a_f \cdot C_R \exp(-K_L a_f \cdot t) \quad (31)$$



240
 241 Fig. 4. Gas Depletion Time Variation ($R > 0$) Modified model

242 This is similar in expression as Eq. (27) above, but with C_R modified to:

243 $C_R = C_{\infty f}^i - \frac{2R}{K_L a_f} \quad (32)$

244 Therefore,

245 $F = R + (K_L a_f \cdot C_{\infty f}^i - 2R) \exp(-K_L a_f \cdot t) \quad (33)$

246 at $t = 0$, therefore,

247 $F = K_L a_f \cdot C_{\infty f}^i - R \quad (34)$

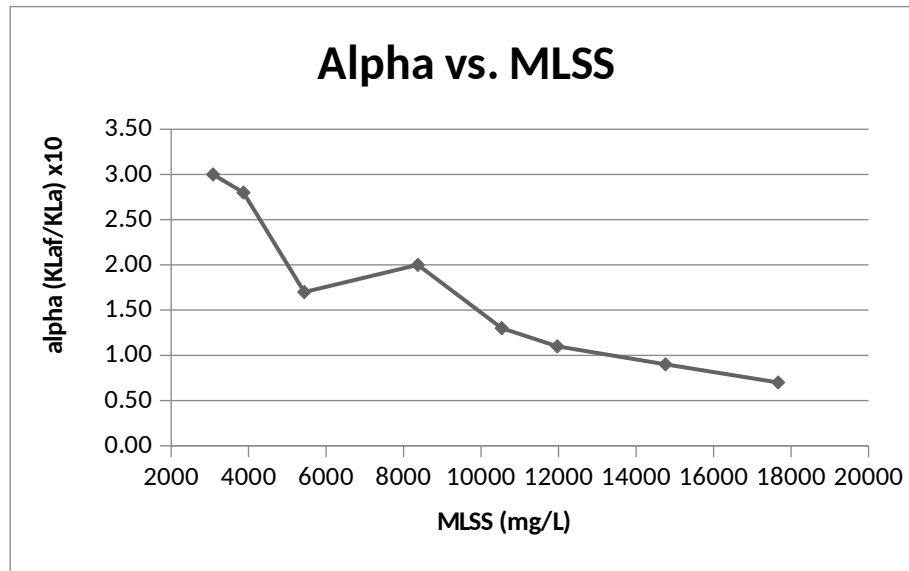
248 at $t = \infty$, $F = R$, the plot then becomes as shown in Figure 4. This plot shows that the initial
 249 depletion rate is reduced by an amount equal to the respiration rate R . Experiments have borne
 250 out the fact that, when respiring cells are present, the initial gas depletion must be smaller than
 251 when cells are absent, as evidenced by the higher off-gas content compared with the non-cell
 252 test. Furthermore, the non-cell condition would give a zero depletion rate at the end when the
 253 off-gas is equal to the feed gas content; whereas, in the case of the oxygen uptake rate (OUR_f)
 254 with R achieving a steady state, the off-gas mole fraction becomes constant at a lower value than
 255 0.2095 (assuming the feed gas is air), and F at steady state equates to the respiration rate R .

256 Since the gas depletion represents the net oxygen transfer, the OTR_f therefore equates to
 257 the consumption by the microbes, as is expected if a steady state is reached under the influence
 258 of the respiring cells. Using the principle of superposition, the *total potential* oxygen transfer rate
 259 remains given by $K_L a_f \cdot (C_{\infty f}^i - C)$ as if the cells are not present (the baseline case), and $K_L a_f$ is
 260 then a fixed constant independent of R and gas depletion. This plot is therefore more correct for a
 261 consistent interpretation of the mass transfer coefficient $K_L a_f$.

262 The conclusion of this exercise is that, for submerged aeration where gas loss rate from
 263 the system is significant, the rate of transfer under the action of microbial respiration should be
 264 given by **Eq. (29)** reproduced below:

265
$$\frac{dC}{dt} = K_L a_f (C_{\infty f} - C) - 2R$$

266 This equation should then replace Eq. (2-2) in the ASCE 18-18 Guidelines. Experimental data
 267 does not exist to verify the gas depletion model as shown in Figure 4, since no data on direct
 268 comparison of a baseline case and a real case ($R > 0$) is available.



269

270 Fig. 5. Relationship between alpha and MLSS for the membrane diffuser at 0.0283 m³/min (1
 271 SCFM)

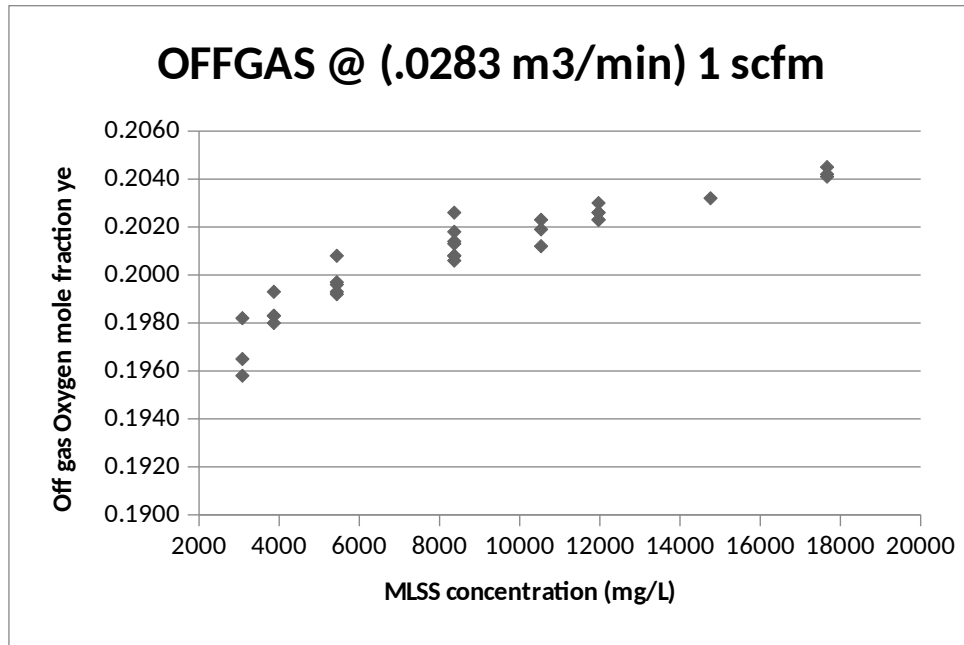


Fig. 6. Relationship between offgas and MLSS for the membrane diffuser at 1 SCFM

However, since R does affect gas depletion at the end of the test, it is logical to assume that R also affects the gas depletion in the beginning of the test making it likely eq. 29 is more representative than the current ASCE model.

Furthermore, if the same gas flow rate is applied, successive tests for estimating α using increasing MLSS (hence increasing steady state uptake rate) will indicate whether the initial gas depletion rate should be diminished by the uptake rate R . This is indeed the case by examining Jing Hu's data [Hu 2006].

His data on the measurements of α and offgas values are plotted as shown in Figure 5 and Figure 6. Figure 5 shows that there is a general trend of decreasing α , hence in Figure 6, a decreasing gas depletion rate or increasing off-gas emission rate is obtained, for increasing MLSS or increasing R . In other words, the effect of R is a suppression of the gas depletion or a suppression of the net oxygen transfer rate in the system.

286 Therefore, as given by eq. 30,

$$287 \quad F = K_L a_f (C_{\infty f}^i - C) - R$$

288 It should be noted in passing that the above plot as shown in Figure 6 is obtained when the offgas
289 data for the same test is plotted against the MLSS [Hu J. 2006]. This phenomenon then agrees
290 with the model that the gas depletion is given by **eq. 30** above, instead of the current ASCE 18-
291 18 model for gas depletion rate given by ASCE's Eq. (3-1) as $F = K_L a_f (C_{\infty f}^i - C)$.

292 *4. Material and Method used on the Case Study*

293 Mahendraker's concept of resistances in series

294 Mahendraker et al. (2005b) postulated that the resistance to oxygen transfer is composed of two
295 elements: the resistance due to the reactor's solution, and the resistance due to the biological
296 floc. They formulated the relationship between these resistances (in which α is not determined by
297 the NSS (non-steady state) method, but by SS (steady state) or off-gas) as:

$$298 \quad \frac{1}{\propto K_L a} = \frac{1}{\propto' K_L a} + \frac{1}{K_L a_{bf}} \quad (35)$$

299 in which the scaling factor for the reactor solution was denoted in their equation by \propto_e ,
300 equivalent to the symbol α' in eq. 35. The subscript for the second resistance bf represents that
301 due to the biological floc. Hence, rearranging eq. 35 gives:

$$302 \quad \propto K_L a = \frac{\propto' K_L a \times K_L a_{bf}}{\propto' K_L a + K_L a_{bf}} \quad (36)$$

303 The conventional model as stipulated by ASCE 18-96 equation 2 [ASCE 1997], or equation 2-2
304 in ASCE 18-18, given by eq. 17 is re-stated below:

305 $\frac{dC}{dt} = K_L a_f (C_{\infty f} - C) - R$ Assuming $K_L a_f = \alpha' K_L a$ and substituting eq. 36 into the conventional
 306 model in a steady state ($dC/dt = 0$; $C = C_R$) and for a batch reactor, and solving for $K_L a_{bf}$ we
 307 have:

308
$$K_L a_{bf} = \frac{\alpha' K_L a \times R}{\alpha' K_L a (C_{\infty f} - C_R) - R} \quad (37)$$

309 If it is assumed that the resistance of the biological floc is identical to the resistance from the
 310 reactor solution, (this is similar to assuming that the *gdp* (gas depletion rate) due to the microbes
 311 is due to the resistance in the bioreactor solution $K_L a_f$), then

312
$$K_L a_{bf} = \alpha' K_L a \quad (38)$$

313 This makes sense as there is no direct contact between the microbial cells and the air bubbles and
 314 so any additional resistance due to biochemical reactions must come from the liquid phase.

Q	$K_L a(\text{eff})$	$1/K_L a$ (eff)	$1/K_L a_{bf}$	$\alpha K_L a$	sp. $K_L a_f$	$K_L a$	α'	α	rpt. α
(1)	(2)	(3)	(3a)	(4)	(5)	(6)	(7)	(8)	(9)
854	7.37	0.14	0.14	3.69	0.053	7.34	1.00	0.50	0.55
1096	8.46	0.12	0.12	4.23	0.052	8.79	0.96	0.48	0.42
854	7.90	0.13	0.13	3.95	0.057	7.78	1.02	0.51	0.60
1096	8.06	0.12	0.12	4.03	0.049	8.86	0.91	0.45	0.58
1320	8.90	0.11	0.11	4.45	0.048	8.74	1.02	0.51	0.54
1945	12.44	0.08	0.08	6.22	0.053	12.36	1.01	0.50	0.42
2140	13.32	0.08	0.08	6.66	0.054	13.51	0.99	0.49	0.39
1320	8.90	0.11	0.11	4.45	0.048	9.61	0.93	0.46	0.61
1320	9.46	0.11	0.11	4.73	0.052	9.81	0.96	0.48	0.46

1540	9.70	0.10	0.10	4.85	0.048	9.57	1.01	0.51	0.41
1320	8.30	0.12	0.12	4.15	0.045	8.28	1.00	0.50	0.39
1540	9.85	0.10	0.10	4.93	0.049	9.57	1.03	0.51	0.35
1645	7.60	0.13	0.13	3.80	0.036	10.69	0.71	0.36	0.39
2311	11.37	0.09	0.09	5.69	0.044	12.72	0.89	0.45	0.39
3475	19.43	0.05	0.05	9.72	0.058	18.36	1.06	0.53	0.26
2657	14.56	0.07	0.07	7.28	0.051	14.66	0.99	0.50	0.36
				avg.=	0.050		0.968	0.48	0.445
				sd=	0.005		0.079	0.040	0.098

Table 1. Data for OUR test vs. non-steady state test (note: avg.=average; sd=standard deviation; rpt.=reported; subscript eff= effluent from reactor) [Mahendraker 2005b]

Substituting eq. 38 into eq. 37 and solving for $\alpha' K_L a$, gives:

$$\alpha' K_L a = \frac{2R}{(C_{\infty}^i - C_R)} \quad (39)$$

Mahendraker et al.'s experimental data [Mahendraker 2005b] is reproduced in Table 1. In the table, Col. 1 is the gas flowrate; Col. 2 is the reported mass transfer coefficient test result on the effluent of the reactor solution using the non-steady state test method ($\alpha' K_L a$); Col. 3 is the reciprocal of Col. 2; Col. 3a is the resistance of the biological floc that is identical in value to the resistance of the reactor solution in Col. 3 (based on eq. 38); Col. 4 is the predicted mass transfer coefficient calculated by eq. 35 ($1/\text{Col. 4} = \text{Col. 3} + \text{Col. 3a}$) giving the calculated value of $\alpha' K_L a$.

Based on a previously developed model, the author was able to calculate the specific mass transfer coefficient (sp. $K_L a$), and this is calculated and stated in Col. 5. As defined by Lee [2018], the specific $K_L a$ is a constant that can be used for scale-up. Since the tests were done in a laboratory scale, the mass transfer coefficients are essentially baseline K_{La0} and so the specific

330 baseline must be constant. With the flow rate given (Col. 1) and $\alpha \cdot K_{La}$ estimated using the model
331 together with the reactor effluent K_{La} , the specific K_{La} as shown in Col. 5 is calculated by
332 dividing Col. 4 by Col. 1 with an exponent of 0.63 after plotting the K_{La} versus Q relationship.
333 [Lee 2018] [Lee 2019a, b]. As one can see, this value is quite constant for all the tests, with a
334 standard deviation of only 0.5%. When the exponent is changed to 0.8, the specific K_{La_f} has a
335 value of 0.014 with a standard deviation of 0.2%.

336 Col. 6 is the measured mass transfer coefficient for the clean water tests as reported
337 [Mahendraker 2003 Appendix D]. Surprisingly, there is little to choose between the clean water
338 data and the reactor solution data (Col. 2). The resulting α -factor' is very close to unity with a
339 standard deviation of around 7.9% as given in Col. 7 calculated by the ratio of the reactor
340 solution $K_{La}(\text{eff})$ in Col. 2 to K_{La} of water in Col. 6. This shows that, without the established
341 oxygen flow path, the resistance is only due to the bulk liquid.

342 The α -factor values stated in Col. 8 (Col.4/Col.6) is based on the resistances-in-series
343 model (eq. 35) but it is still based on the conventional concept for α . In the new concept, true
344 alpha should be α' . Col. 9 is the reported alpha-factor obtained from the off-gas or SS test result
345 where K_{La_f} ($\alpha \cdot K_{La}$) is calculated by the conventional formula [ASCE 2018].

346 For comparison, the model seems to give more consistent result (Col. 8) compared with
347 Col. 9. The reported α -factor values (Col. 9) calculated from the 'erroneous' mass transfer
348 equation are almost 50% less than α -factor' (Col. 7) based on the non-steady state test method
349 and therefore Col. 9 values must not be accepted. By the same token, Col. 8 values should not be
350 accepted either for the estimation of OTR_f . However, direct comparison of the OTR (NSS vs.
351 off-gas SS) is not possible without including the respiration rate R that is required to calculate
352 K_{La_f} with the new equation (eq. 29). It is very clear from Mahendraker's work that there is a

huge discrepancy between the various testing methods. As a separate exercise, the reported R values in Mahendrakar [2003] were scrutinized and re-used to calculate the net transfer efficiency (OTE_{pw}), but the R data values suffered the same fate of an elevated respiration rate as for a BOD bottle-based test, because they were determined in a respirometer subjected to agitation and forced aeration of the sample prior to measurement. However, when the R value was adjusted to some 50% of the respirometry result prior to re-calculation, the overall discrepancy in the estimation of $K_L a_f$ is around 12% and not 50% as reported [Lee 2019a], bearing in mind that Mahendrakar's test is a continuous flow process and not a fed-batch process. The experimental error induced by the off-gas technique, as well as the correction of around an average of 50% in the respirometry results can be such, so that this overall error of 12% is considered satisfactory. This example shows that the new concept of a resistance (eq. 6) leading to eq. 8 is correct --- there really is an additional force that constitutes an energy loss leading to a reduction of gas transfer due to the presence of microbes in the mixed liquor.

The current concept as postulated in this paper applied to the same data

Alternatively, using the steady-state method and the proposed model when the system has reached a steady state in the presence of microbes, the gas depletion rate is a constant, and so it would be possible to calculate the *microbial gdp* by the same equation (eq. 8) and by incorporating R as well when $dC/dt = 0$ and $C = C_R$. In the presence of microbes, the mass balance equation is given by eq. 7. The advocated hypothesis is that this gdp_f due to the microbes is the same as the reaction rate R leading to $dC/dt = K_L a_f (C^*_{\infty} - C) - R$, compared to clean water where the microbial $gdp = 0$. In other words, if F_1 is the gas depletion rate for clean water, and F_2 is the gas depletion rate in process water, then $F_1 - F_2 = R$. It should be noted that, as mentioned before, the basic mass transfer equation is universal, its general form given by the form

376 manifested by Eq. (4). Therefore, in a non-steady state test for in-process water for a batch test,
377 the transfer equation is given by:

$$378 \quad \frac{dC}{dt} = K_L a_f (C_R - C) \quad (40)$$

379 where C_R is the “*apparent*” saturation concentration or the “*pseudo*” steady-state DO value in the
380 test tank at the in-situ oxygen uptake rate, R . But the transfer equation is also given by $dC/dt =$

381 $K_L a_f (C_{\infty}^i - C) - R$. Equating the two gives,

$$382 \quad K_L a_f (C_{\infty}^i - C) - R - R = K_L a_f (C_R - C) \quad (41)$$

383 which gives:

$$384 \quad K_L a_f = \frac{2R}{(C_{\infty}^i - C_R)} \quad (42)$$

385 When both measurements are plotted against the model, as shown in Fig. 7, it can be seen that the
386 reactor effluent almost exactly coincides with the two-resistance model prediction, but the
387 conventional model when used in a steady-state in-process setting gives a correlation that is
388 somewhat skewed to 50% of the reactor solution, as shown by the lower graph in the figure.

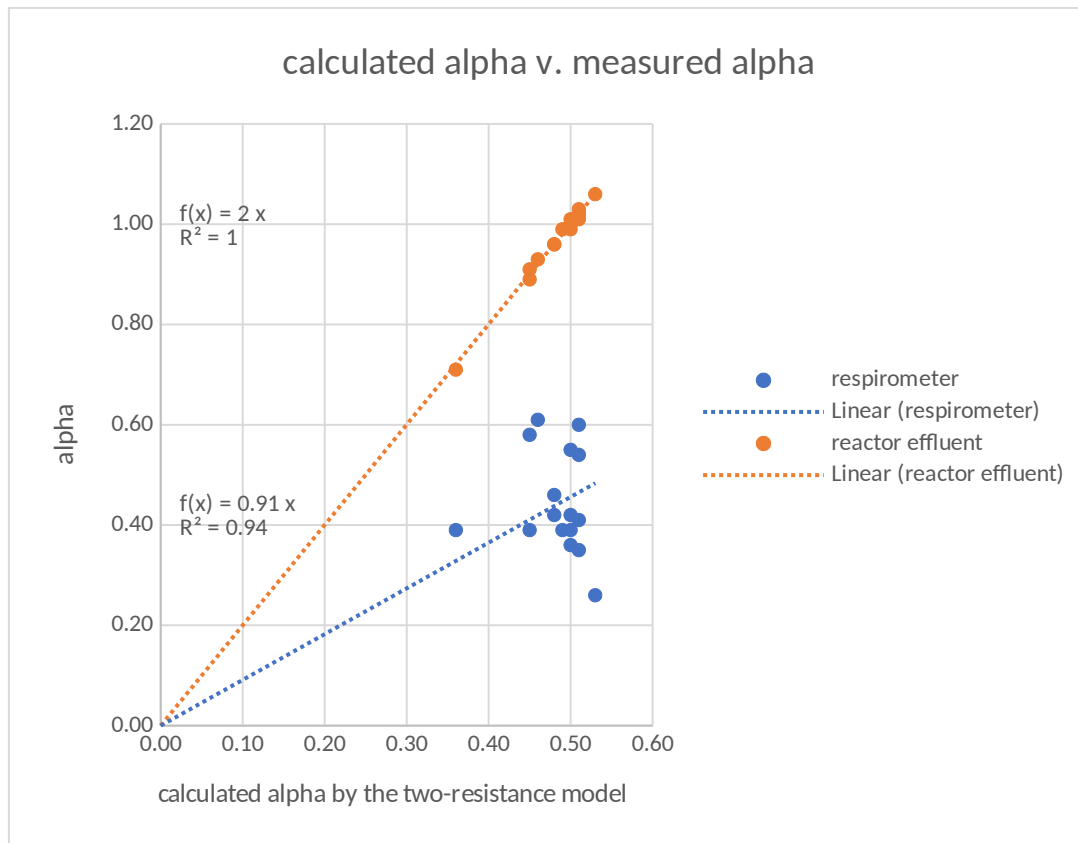


Fig. 7. Comparion of alpha-factors

Eq. 42 is identical to eq. 39 derived using Mahendraker's principle. Note that in this equation (eq. 42), C is cancelled out, so that the above equation is valid for any value of C , at any state, so long as $dC/dt > 0$ and $C < C_R$. This equation shows that K_{La_f} should really be given by $\alpha'K_{La}$ and not $\alpha.K_{La}$, when it is accepted that the resistance due to the microbes (the biological floc) is the same as the resistance from the reactor solution (eq. 38).

5. Discussions

"The higher the reaction rate, the smaller the gas depletion rate". This phrase is at first difficult to understand because in an aerobic process if reaction rate increased, the oxygen consumption will be higher (the oxygen is needed to degrade organic matter) and gas depletion should be higher", but this can be readily understood when a gas phase mass balance of oxygen

401 is taken over a liquid volume when the system is at steady state. The difference between the feed
402 gas rate and the exit gas rate must be the oxygen transfer rate (OTR), which is equal to R ; but the
403 OTR is also the gas depletion rate, and so the microbial gdp must also equal to R . The text
404 simply means that, for the same gas supply rate (therefore constant K_{La_f} during the duration of
405 the study), an increase of R such as an organic shock load, adds an additional resistance and so
406 the microbial gdp would increase, but the overall gdp or OTR would decrease, requiring the
407 system to adjust to a new steady-state by lowering the steady state DO concentration C_R , thereby
408 increasing the driving force so that the OTR_f would match the new oxygen demand.

409 However, if C_R becomes too low, the blowers might then need to work harder, not only to
410 constantly provide enough air to maintain the oxygen being consumed by the biomass (oxygen
411 uptake rate $OUR_f = R$), but also to maintain a stable ‘spare’ DO level required to overcome the
412 additional resistance. In this case, the gdp would obviously increase to counteract the increase in
413 R , but the gas flow rate Q_a would also be different and then it would violate the limitations of the
414 test [ASCE 1997] [ASCE 2018], as change in the gas flow rate means that K_{La_f} is no longer
415 constant. In another experiment on the performance of a membrane bioreactor (MBR) treating
416 high strength municipal wastewater, conducted by Birima et al. (2009), the results of dissolved
417 oxygen (DO) and aeration rate show that the effect of the organic loading rate (OLR) on aeration
418 rate and DO concentration was very significant. For instance, comparing the results of a trial
419 with low OLR with those of another trial with high OLR shows that the aeration rate in the first
420 trial was 20 L/min corresponding to DO of above 4 mg/L, whereas, the rate of aeration in the
421 second trial increased rapidly till 60 L/min but corresponding to a DO of below 2 mg/L.
422 Similarly, for other trials, it was noted that the higher the organic loading rate, the higher would
423 be the aeration rate and correspondingly the lower the DO concentration. Since the K_{La} is an

increasing function of the aeration rate [Lee 2018] [Lee 2019a], it would appear as if the transfer capacity has increased.

This is not an enhancement effect allegedly due to direct bubble contact, as Albertson and DiGregorio [1975] surmised, who reported that the field K_La values are dependent on the biological oxygen uptake rate R and increase as R increases.

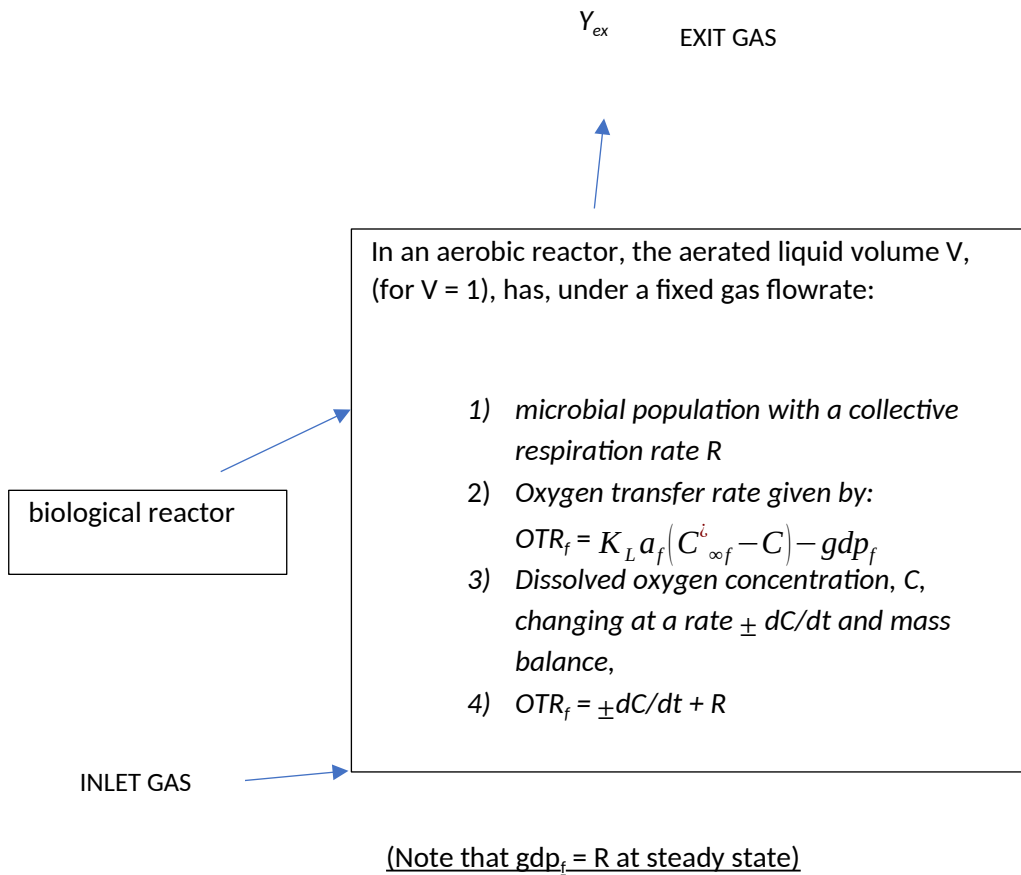


Fig. 8. Mass Balance on the gas phase

In this manuscript, we propose that, previously, the K_{La_f} was estimated based on an incomplete equation [ASCE 1997, 2018] that has neglected the effect of a microbial gas depletion rate. We propose that K_{La_f} is in fact not dependent of R but the OTR is, so that the transfer equation

should be amended to include the microbial resistance (the respiration rate R) as an additive quantity as Figure 8 self-explains.

We postulate that this gas depletion effect is not part of a scalar quantity to be attached to the clean water mass transfer coefficient as a correction factor. This observation by Birima et al. (2009) of an increased oxygen transfer in fact supports the hypothesis of a higher resistance to oxygen transfer when the demand for oxygen has increased, even though the driving force has increased because of the lowered DO. This implies that for higher organic load, a higher rate of aeration is required to obtain the same DO. This means that operating the MBR with a high organic load means that more energy is required. The overall OTE (Oxygen Transfer Efficiency) for any gas supply rate is still a downward trend under high demand conditions for that specific gas SUPPLY rate. Generally, the results of the study showed that for the low OLR trials the aeration rate varied from 6 to 12 m³ /m² membrane area per hour and the DO varied from 3.7 to 5.7 mg/L, whereas for the high OLR trials the aeration rate and the DO varied from 6 to 18 m³/m² membrane area per hour and 0.9 to 4.4 mg/L, respectively. This depends on the concentration of MLSS in the reactor that in turn directly affects the respiration rate of the microbial communities. The effect of the aeration rate (and their associated mixing intensity) on OTE should be further investigated.

It is no doubt desirable to have new experimental data to verify the hypothesis of $2R$ in the mass transfer equation under microbial metabolism, but Mahendraker's data unequivocally proved that there is a resistance to oxygen transfer, along with other researchers' finding, such as Cambell (2020) cited above. When the microbes are not inserted, the only resistance is the reactor solution, giving a resistance of $1/K_L a_{(\text{effluent})}$. When the pathway is mobilized by the presence of microbes drawing down the DO concentration gradient (the driving force), the resistance is

466 increased substantially. This can be confirmed by the reduction of the OTR by measuring the off-
467 gas rate or the OUR at steady-state, either using a respirometer or something similar, the
468 accuracy of such device notwithstanding. The result of this pathway usually gives a calculated
469 K_{La_f} much lower than would be obtained without, using the conventional equation with a single
470 R . This paper postulates that a much better match would be obtained if we only separate the
471 effect of gas-side gas depletion as an additive-associative factor, rather than as part of a scaled
472 factor attached to K_{La} . The first resistance always exists so long as there is bubble aeration,
473 where Lewis and Whitman (1924) two film theory always applies. The mechanism of transfer
474 switches predominantly to a reduction of mass transfer rate, as exemplified by the reduction in
475 concentration gradient ($C_R - C$) when the element of microbial respiration is added, especially
476 when under a high organic loading rate and/or a low DO level situation, and this resistance exists
477 only when living cells exist in the aqueous solution. A simple experiment using synthetic
478 substrates such as yeast carried out in a bench scale batch reactor will illustrate the
479 point[Mahendraker et al. 2005a]. When the bioreactor has reached steady state, the DO
480 concentration will reach C_R and $dC/dt = 0$. A sample can be collected from the supernatant and
481 the microbial uptake rate can be determined as per the Standard Method [Standard Methods
482 2017] if the DO is sufficient to allow testing without shaking or agitating to provide artificial re-
483 aeration. If not, the sample should be diluted with pre-aerated water so that sufficient DO can be
484 attained prior to the OUR test. The result will then provide an estimate of K_{La_f} using eq. 2-2 of
485 ASCE 18-18.

486 Simultaneously, another sample is collected and then de-oxygenated by nitrogen if
487 possible [ASCE 2007]. The sample is then re-aerated until steady state is reached. From the non-
488 steady state re-aeration, an oxygenation profile can be obtained. By using the non-linear least

squares technique to fit the data, a best-fit estimate of the $K_L a_f$ can be obtained. If the mass transfer equation is correct, the two $K_L a_f$ values should be the same. However, if they differ by 50% or so, then the ASCE eq. 2-2 is confirmed to require correction to take into account of the gas-side oxygen depletion effect as postulated in this paper.

6. Conclusion

It has been widely concluded in the scientific community that clean water testing is of limited usefulness, except for comparison of aeration equipment at full scale. The discrepancies between anticipated and actual performance are often sufficiently large to warrant substantial field modifications to the aeration equipment furnished as may generate ill will between the supplier and owner. [Brenner R.C. 1979]. According to Stenstrom and Gilbert (1981), the scale-up of test equipment seems to dramatically affect the determination of the alpha-factor (α) which is the relative mass transfer coefficient ($K_L a$) of in-process water compared to clean water. Furthermore, $K_L a$ has been alleged to be related to the biological uptake rate in respiring systems. [Albertson and DiGregorio (1975)][Hwang and Stenstrom 1985][Vaxelaire J. et al. (1994)] To overcome this shortfall of the clean water test, a rigorous theoretical analysis of the oxygen transfer mechanism has been carried out and it is proposed that the current equations be modified to include this microbial effect, and the new equations for scaling up to field conditions have already been stipulated in a previous paper.[Lee 2018].

The main theme of this case-study paper is that, the alpha-factor α must not be attached to the microbial effect, but must be decisively related to wastewater characteristics, which depends on substrate loading, sludge age, the amount of suspended solids and other characteristics. It is suggested that eq. 1 contains both an energy balance and a mass balance bundled into one single equation that makes the interpretation of the mass transfer coefficient untenable. The alpha-

factor (α) implicit in this equation is dependent on the microbial activity as well as the wastewater characteristics. It is postulated that the ratio OTE_{pw}/OTE gives only a false alpha, where the subscript pw stands for process water undergoing biological stabilization due to microbial metabolism. In order to separate the two effects, this paper has shown that the correct oxygen transfer equation should be written as eq. 29 re-stated below:

$$\frac{dC}{dt} = K_L a_f (C_{\infty f}^i - C) - R - R$$

where $K_L a_f$ should be given by $\alpha' K_L a$. By equating eq. 1 to eq. 29, it can be seen that the relationship between the two alpha's is given by:

$$\alpha = \alpha' - \frac{R}{K_L a (C_{\infty f}^i - C)} \quad (43)$$

WHERE α PERTAINS TO $K_L a_f$ IN THE OLD EQUATION, AND α' PERTAINS TO THE NEW EQUATION. ONE CAN SEE THAT, IN THE OLD EQUATION, THE ALPHA-FACTOR IS DEPENDENT ON THE MICROBIAL ACTIVITY; WHILE IN THE NEW EQUATION ALPHA ($\alpha = \alpha'$) IS ONLY RELATED TO WASTEWATER CHARACTERISTICS WHICH THEN GIVES IT A MUCH MORE CONSISTENT MEANING, SINCE THE MICROBIAL EFFECT IS HIGHLY VARIABLE AND DEPENDS ON MANY THINGS.

The field-determined OTE_{pw} is affected by the respiration rate R that is dictated by the microbial activity, which is mathematically associative to the transfer process by addition (based on the superposition principle), and not associative by multiplication with a scalar quantity. A gas-phase mass balance for oxygen around a completely mixed aeration tank confirms the association nature of the alpha-factor. This is the most important distinction between OTE_{pw} and OTE_f in any attempt to translate clean water test results to wastewater oxygen transfer. Examination of test data extracted from the literature indicates that this is indeed the case.

This way, together with a proven scale-up equation (Lee 2018) to account for water depths and geometry for the calculation of $K_L a_f$ and $K_L a$ at full-scale, it is hoped that the actual oxygen field

transfer rate can be estimated *a priori* with better approximation than before, provided that the oxygen uptake rate and the alpha-factor can be determined in a laboratory or bench scale *a priori* as well.

Data Availability Statement

All data, models, and code generated or used during the study appear in the submitted article.

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