

EXPERIMENTAL DETERMINATION OF THE VOLUMETRIC MASS TRANSFER COEFFICIENT

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ABSTRACT

The volumetric mass transfer coefficient (k_La) is often used in order to compare the efficiency of bioreactors and as an important scale-up factor. In bioreactors, a number of methods are available for estimation the overall volumetric oxygen mass transfer coefficient: the dynamic method, the steady-state method based on a preliminary determination of the oxygen uptake rate, the gaseous oxygen balance, the carbon dioxide balance. Each method provides a different estimation of the value of k_La . We examined the sensitivity of the various methods and compare the k_La values obtained in order to select the most suitable method as a function of the type of bioreactor used. In this work we applied dynamic gassing-out method for measuring the volumetric mass transfer coefficient k_La in three type gas-liquid reactors (stirred tanks, bubble columns and airlift). The aim of this work is on the basis of our experimental data to obtain several correlations for evaluation of k_La .

Keywords: volumetric oxygen transfer coefficient, bubble columns, CSTR, airlift reactors.

INTRODUCTION

Aeration and agitation are important variables to provide effective oxygen transfer rate during aerobic bioprocesses. Hence, the knowledge of the volumetric mass transfer coefficient (k_La) is required. The determination of k_La in a bioreactor is essential in order to establish its aeration efficiency and to quantify the effects of operating variables on oxygen supply.

Oxygen transfer in aerobic bioprocesses is essential and any shortage of oxygen vastly affects the process performance. Therefore, oxygen mass transfer is one of the most important phenomena in the design and operation of mixing-sparging equipment for bioreactors [4]. It can be described and analyzed by means of the volumetric mass transfer coefficient, k_La . The values of k_La are affected by many factors, such as geometrical and operating characteristics of the reactor (type of impeller, the geometry of the bioreactor, the agitation speed and the air flow rate), media composition and properties, concentration and microorganism's morphology and

biocatalyst's properties [3].

In aerated systems the critical limiting factor in providing the optimal environment is the oxygen transfer rate (OTR). The mass balance for the dissolved oxygen in the well-mixed liquid phase can be written as:

$$\frac{dC_L}{dt} = k_La(C_L^* - C_L) - r_{O_2} = OTR - OUR \quad (1)$$

When oxygen uptake rate, $OUR = 0$, the oxygen mass balance in the liquid phase can be simplified to:

$$\frac{dC_L}{dt} = k_La(C_L^* - C_L) = OTR \quad (2)$$

or

the oxygen mass transfer rate can be described as proportional to the concentration gradient. For aerobic fermentation the maximum value of the concentration gradient is limited due to the low solubility of oxygen. Therefore, the maximum mass transfer rate from the gas to the liquid in the bioreactor can be estimated by $k_La.C_p$

as C_L^* is the saturation concentration in the liquid phase.

Integrating:

$$\int_{C_{L1}}^{C_{L2}} \frac{1}{(C_L^* - C_L)} dC = k_L a \int_0^t dt \quad (3)$$

$$\ln \left(\frac{C_L^* - C_{L1}}{C_L^* - C_{L2}} \right) = k_L a t \quad (4)$$

Hence a plot of of

$$\ln \left(\frac{C_L^* - C_{L1}}{C_L^* - C_{L2}} \right)$$

vs. t should result in a straight line of slope $k_L a$.

METHODS

The methods for measuring the $k_L a$ can be classified depending on whether the determination is made in the

Table 1. Methods for volumetric mass transfer coefficient determination [2].

Measurement method		$k_L a \cdot 10^2$ [s ⁻¹]	Assay time	Scale applied	Assumptions/Drawbacks
Chemical	Sulfite oxidation	0 - 0,3	Hours	Laboratory scale	The rate of reaction is assumed to be zero order in sulfite. Alteration of driving force, diffusion coefficient, and coalescence properties; complex kinetics boundary layer reduction. This method is fairly labor intensive.
	Absorption of CO ₂	0 - 0,1	Minutes	Laboratory scale	Assumptions about kinetic reaction must be made. Possible alteration of the driving force. Change of the coalescence behavior.
	Dynamic measure of pH	0 -0 ,03	Half an hour	Any scale	Assumptions about kinetic reaction must be made. Salt addition does not alter the mass transfer rate of CO ₂ .
	Hydrazine oxidation	0-0,5	Minutes	Pilot plant	Hydrazine does not accumulate. No chemical enhancement.
	Bio-oxidation of catechol	< 0,8	Minutes	< 100ml	Available of oxidative enzyme; limited to small scales.
Physical	Dynamic	0 - 0,1	Minutes	>100 ml	A nonrespiring system can be employed to simulate the fermentation broth. The response time of the electrode, τ_r , is a critical parameter. Gassing time can be significant at larger scales
Biological	Biological Dynamic gassing out	0 - 0,1	Minutes	Any scale	High DO concentration is necessary. Nongassing period must be short and OUR independent of DO concentration. Invasive probes are necessary and response time must be considered. Hydrodynamic changes may disturb the microbial metabolism.
	Biological dynamic method with high OUR	0 - 0,1	Minutes	Any scale	OUR is independent from DO concentration. Invasive probes are necessary and response time must be considered
	Gas phase analysis	0 - 0,3	Hours	>100 ml	For large scales, the assumptions of well-mixed gas and liquid phase may not be valid. This method may not be the best choice in case of small bioreactors, where the difference between F_{in} and F_{out} may be very small because of the short contact time The accuracy depends on the precision of oxygen analyzer

Table 2. Corellations for volumetric mass transfer coefficient calculation in the literature.

Authors	Type	Corellation	System
Kapic and Heindel [3]	STR Rushton impeller	$k_L a = 0,04 \left(\frac{P}{V} \right)^{0,47} U_G^{0,6}$	Air-water
Moucha et al [4]	STR Rushton impeller	$k_L a = 1,081 \cdot 10^{-3} (P_{tot}/V_L)^{1,19} U_G^{0,549}$	Air-water
Yawalkar1 et al [5]	STR Rushton impeller	$k_L a = 3,35 (rpm/rpm_{min})^{1,19} U_G^{0,549}$	Air-water
Garcia-Ochoa and Gomez [2]	STR	$k_a a = 6,66 \times 10^{-4} \left(\frac{P}{V} \right)^{0,6} U_G^{2/3} \mu^{-2/3}$ $k_a a = 17,20 \times 10^{-4} N^{2,0} U_G^{2/3} \mu^{-2/3}$	Air-water
Akita and Yoshida [6]	Bubble column	$k_L a = d_c^{0,17} U_G^{0,7}$	Air-water
Deckwer et al [7]	Bubble column	$k_L a = 0,0296 U_G^{0,82}$	Air-water
Hikita et al [8]	Bubble column	$k_L a = 14,9 D_L^{0,60} \sigma^{-1,02} \mu_L^{-0,08} \mu_G^{0,24} \rho_L^{0,85} g^{0,75} U_G^{0,76}$	Air-water
Sada et al [9]	Bubble column	$k_L a = c U_G^{0,86}; c = f(solution)$	Air-water
Bello et al [10]	Airlift External loop	$k_L a = 0,79 [1 + A_d/A_r]^{-2} U_G^{0,8+0,1}$	Air-water
Karimi et al [11]	Airlift Internal loop	$k_L a = 0,1107 [1 + A_d/A_r]^{-2} U_G^{0,8979}$	Air-water
Sánchez Mirón et al [12]	Airlift Internal loop	$k_L a = 0,837 U_{GR}^{0,971}$	Air-water
Choi et al [13]	Airlift Internal loop	$k_L a = 0,176 U_{Gr}^{0,761} (A_d/A_r)^{-0,056} (L_c/L_h)^{-0,168}$	Air-water

absence of microorganisms (chemical and physical methods) or in the presence of biomass (biological methods). In Table 1 are summarized methods for the volumetric mass transfer coefficient determination. Chemical and biological methods require a reaction in the liquid phase to reduce the dissolved oxygen (DO) concentration to a level below saturation. The most often used chemical method is chemical oxidation, and from biological methods - cellular respiration. The physical methods are based on the measurement of the oxygen concentration in the liquid or in the exhaust gas flow during absorption/desorption process. The methods differ in the procedure of gas interchange, in the gas used, and in the model for the gas-phase description [2].

EXPERIMENTAL

The $k_L a$ was determined by physical dynamic method as described by Benyahia and Jones [14]. The activated sludge liquid was deoxygenated by stripping with nitrogen. Then, nitrogen was replaced by air, and the dissolved oxygen concentration in the liquid was measured until equilibrium was reached. The air flow was uninterrupted during the switch from nitrogen to air so that the consistent fluid dynamic conditions were maintained in the reactor throughout the experiment. When $k_L a$ is considered to be independent of time, integration of equation with $C_L = 0$ at $t = 0$ gives:

$$C_L(t) = C_L^* \left(\frac{1 - \exp(-k_L a t)}{t} \right)$$

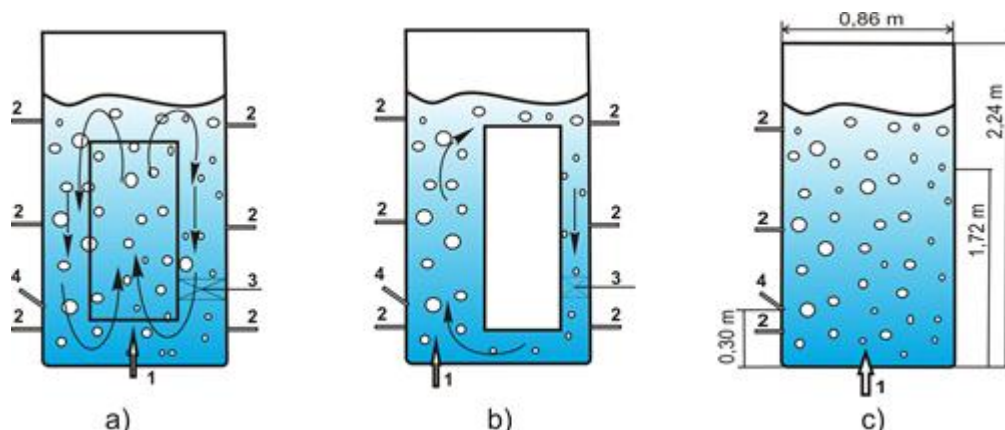


Fig. 1. Schematic diagram of the airlift reactors with a) internal circulation, b) external circulation, c) bubble column: 1 –air distributor; 2 – manometers; 3 – liquid circulation velocity measure; 4 – DO probe.

The values of $k_L a$ were determined from the slope of the straight line obtained from a plot of $\ln(C_L^* - C_L)$ against the time. This method for evaluation of $k_L a$ is applicable when assuming a well-mixed liquid phase, a constant air concentration along the column height and a fast response of oxygen electrode to a change in the dissolved oxygen concentration.

Stirred tank, bubble column and airlift reactor were used to conduct experiments for $k_L a$ determination using of a dynamic gassing-out method.

Stirred tank reactor: measurements were performed in six pitched turbine stirred fermentors with total volume

50 l (35 l working volume, d/D ratio = 0.375) and 1300 l (1000 l work volume, d/D ratio = 0.6).

Bubble columns reactors: the experiments were made with 3 different bubble columns. The first one – with total volume 50 l and 35 l working volume, the second – with 85 l total volume and 58 l working volume, and the third – 1300 l and 1000 l total and work volume, respectively. Airlift reactor: measurements have been carried out in the pilot-plant size airlift reactor, riser with 3 m height (H_r), diameter $d_r = 0.2$ m and downcomer with $H_d = 2.8$ m and diameter $d_d = 0.06$ m, working volume $V = 0.062$ m³; $A_d/A_r = 0.09$, where A_d and A_r are downcomer

Table 3. Experimental results.

Reactor type	Total volume [l]	Work volume [l]	H, [m]	d, [m]	A [m ²]	d/H	Impeller	d_d/d	Derived correlation/ Estimated values for $k_L a$
Stirred tank	50	35	0.5	0.36	0.102	0.72	Six pinched turbine	0.375	$k_L a = 0,0638.rps^{0,165}$
	1300	1000	1.68	1	0.785	0.6	Six pinched turbine	0.3	$k_L a = 0,0147.rps^{0,8858}$
Bubble column	50	35	0.5	0.36	0.102	0.72	-	-	$k_L a = 0,4637.U_G^{0,8414}$
	85	58	3	0.19	0.028	0.06	-	-	$k_L a = 0,2096.U_G^{0,7661}$
	1300	1000	1.68	1	0.785	0.6	-	-	$k_L a = 0,4496.U_G^{0,8802}$
Airlift with external loop	92	62	3	0.2	0.031	0.06	$d_d, [m]$	A_d/A_r	$k_L a = 1,1458.U_G^{1,1708}$
							0.06	0.09	

and riser cross-sectional area, respectively. More details are given in Table 3.

In all experiments as a gas phase was used air and desalted water and tylozin as a liquid phase. The oxygen concentration is followed with a P2 – type dissolved oxygen probe and a 703P polarographic oxygen meter from Uniprobe. The probe was located at 300 mm from the bottom of the column at an angle of 45°.

RESULTS AND DISCUSSION

The experiments were carried out in STR at 300 rpm stirring speed and gas phase flow rate 0.25 l/s. The value of $k_L a = 0.076 \text{ s}^{-1}$ was obtained by comparison of the numerical results from model solution and the experimental data for dissolved oxygen concentration [15]. It is obvious that the values of $k_L a$ are not so sensible to the variation of the input air flow rate in comparison with variation of the agitation speed, especially in large reactors. Experimentally obtained values of $k_L a$ in bubble column with work volume 1000 l and 35 l are 0,069 s^{-1} and 0,066 s^{-1} , respectively [16].

In Table 3 are presented experimentally obtained correlations for evaluation of $k_L a$.

CONCLUSIONS

The most suitable method selection for $k_L a$ measurement requires to take into account the range of the variables as power input, volume and type of the reactor, characteristics of gas and liquid phase. The dynamic oxygen method is the most widely used, with a small degree of approximations for gas–liquid mixing in the reactor. This method is suitable for large scale bioreactors with errors less than 10 %, over the entire range of the operating conditions encountered in the industrial fermentor operations.

The steady state sulfite method is not recommended as it gives inaccurate values in comparison with the other methods applied in industrial scale. The use of pure oxygen for accurate estimation of the volumetric mass transfer coefficient is highly uneconomical when other methods are available with a sufficient degree of accuracy.

The response methods are also found to be satisfactory when applied to stirred vessels. Their applicability for media with high viscosity and non-coalescing fermentation

media have to be tested.

On the base of our experimental data empirical correlations were developed for calculation of $k_L a$ values. It was found that the predicted $k_L a$ values were sufficiently well comparable with the observed, especially in small scale stirred tank reactors.

Nomenclature

A_d	downcomer cross-sectional area [m ²]
A_r	riser cross-sectional area [m ²]
C	oxygen concentration [kg.m ⁻³] or [-]
d	diameter [m]
$k_L a$	volumetric mass transfer coefficient [s ⁻¹]
H	length of the reactor [m]
U	velocity [m.s ⁻¹]
V	volume [l]

Subscripts

d	downcomer
G	gas
L	liquid
r	riser

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