Mass transfer coefficient evaluation for lab scale fermenter using sodium sulphite oxidation method

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Abstract - Oxygen transfer is often the rate-limiting step in the aerobic bioprocess due to the low solubility of oxygen inside the aqueous solution. The rate of reaction is such that as oxygen enters the liquid phase, it is immediately consumed to oxidize the sulfite so that the rate of oxidation is equivalent to the oxygen-transfer rate. Reaction rate often determined by titration is much faster than oxygen transfer rate so that gas- liquid mass transfer is the rate controlling step. The current study involves using central composite design, a statistical technique to find out the parameter conditions for the optimum volumetric mass transfer coefficient in a lab scale (2L) fermentor. The optimum volumetric mass transfer coefficient was found to lie outside the range of parameters studied and analytical expressions was obtained to predict the volumetric mass transfer coefficients for the parameter ranges studied using response surface methodology. The analytical expression was found to be significantly valid based on ANOVA results.

Keywords: Aerobic bioprocess; Sodium sulphite oxidation process; Mass transfer coefficient; Central composite design

INTRODUCTION

In aerobic fermentation processes, oxygen is an important nutrient/substrate for the growth, maintenance and production of metabolites. However, oxygen is sparingly soluble in aqueous and/or fermentation media due to its low solubility. Hence, oxygen needs to be supplied continuously during the fermentation. Oxygen transfer rate into the fermentation media and oxygen uptake rate by microorganisms govern the design and scale-up of fermenters [1]. Since one has little control on the oxygen uptake rate governed by microorganisms, it is necessary to enhance the rate of transfer of oxygen into the fermentation medium. The transfer of oxygen into the liquid is usually accomplished by sparging air or oxygen into the medium. Gas-liquid film theory, it can be stated that the oxygen mass transfer rate is limited by the resistance of the liquid film surrounding the gas bubbles which in turn limits the volumetric mass transfer coefficient. Volumetric mass transfer coefficient is the product of liquid mass transfer coefficient and the interfacial area. Interfacial area is difficult to measure and is usually lumped with the liquid mass transfer coefficient to get the volumetric mass transfer coefficient. To explain the mass transfer of gases into liquid, several theories such as Whitman's two-film theory according to this theory equilibrium is assumed based on rigid interface and the resistances to mass transfer in the two phases are added to get an overall resistance, Higbie's penetration theory-there is a continual attachment and deattachment of small liquid eddies at the gas-liquid interface, in the interval of attachment there is a interchange of solute by molecular diffusion, eddies from a turbulent bulk fluid, come to within a random distances of the surface, gives slightly higher exponents for the diffusivity, which indicates this theory might apply for mass transfer to flat surfaces such as pool of liquid, Higbie's was the first to apply this equation to gas absorption in a liquid , showing diffusing molecule will not reach the other side of a thin layer if the contact time is short $Kc = 1.13 \sqrt{(D/t)}$. Danckwert's surface renewal theory here elements of fluid at the transfer surface are randomly replaced by fresh liquid from bulk stream the surface renewal rate is considerably higher than that found for bubbles in free rise under potential flow An exponential distribution of ages or contact times , the average transfer coefficient is given by $Kc = \sqrt{(D \times s)}$. Where D is diffusivity of gas in a liquid is fractional renewal rate [1-3]. In (1951) a combination of these theories has been proposed for prediction of mass transfer coefficient. However, parameters such as film thickness for Whitman's two film theory, exposure time for

Higbie's penetration theory and surface renewal rate for Danckwert's surface renewal theory cannot be measured experimentally and has to be calculated if mass transfer coefficient value is known [4]. This technique is interesting for studying the influence of operational conditions on the volumetric mass transfer coefficient, and is widely employed in the literature. Nevertheless, it is necessary to take into account that the response time of the electrode, τr, is a critical parameter for the determination of accuracy values of oxygen concentration. This response can affect the correct determination of the mass transfer coefficient if the time characteristic for the oxygen transport, $1/kLa$, is of the same order than the response time of the electrode, defined as the time necessary to reach 63% of the final value of measured when exposed to a step change concentration The response time of the electrode can be determined by transferring the oxygen electrode from a solution with sodium sulfite (whose oxygen concentration is zero) to another dissolution saturated with air (100% of saturation). In the case when the electrode of oxygen has a high value of response time it would be necessary to introduce a correction in the response model are available to experimentally determine the volumetric mass transfer coefficient. The most widely used is the sulphite oxidation method. The sulphite oxidation method tends to give higher values for the volumetric mass transfer coefficient and the order of the reaction depends on the concentrations of the sulphite and catalyst. (Usually a divalent cation of Cu^{++} or Co^{++}). In order to obtain an adequate reaction rate, avoiding acceleration of oxygen uptake due to the chemical reaction.

The aim of this study is to predict volumetric mass transfer coefficient based on parameters both physical and chemical viz., impeller speed and air flow rate. For sodium sulphite oxidation method, Central composite design was used to optimize the volumetric mass transfer coefficient for both impeller speed and air flow rate. The rate of dissolution of gas inside the liquid solution is studied by knowing the reaction kinetics and mass transfer theories.

MATERIAL AND METHODS

Sodium Sulphite Oxidation Method

Sodium sulphite oxidation method was first developed [5]. This method is based on the reaction of sodium sulfite, a reducing agent, with the dissolved oxygen to produce sulfate, in the presence of a catalyst (usually a divalent cation of Cu^{++} or Co^{++}). 0.003 M of copper sulphate solution was prepared in 1 L of de-mineralized water which was then transferred to the fermentor vessel. Agitation was started immediately at the required rpm. To this was added 1 L of 0.05 M sodium sulphite . Molecular weight of copper sulphate =126. Weight of copper sulphate = 6.3 gm. simultaneously, air was pumped into the solution via a sparger continuously. The oxygen in the air was immediately consumed by the sulphite oxidation [1,2] Since the reaction rate is much faster than the oxygen transfer rate, so the limiting factor is the oxygen transfer rate [6]. When the dissolved oxygen concentration reached 0% saturation, the remaining unreacted sodium sulphite reacted with oxygen until no more sodium sulphite was present in the solution. Air was pumped continuously till the oxygen concentration in the fermentor reached 100% saturation. At regular intervals of time, a sample was withdrawn from the fermentor. The sample was mixed with an excess of iodine reagent. weight accurately 2 gm, sodium sulphite of concentration 0.05(M), add excess iodine solution which reacts with unconsumed sulphite. The amount of residual sulfite can be also estimated indirectly by the stoichiometry of the reaction on basis of colorimetric determination of the iodine concentration. The sample was then titrated with standard sodium thiosulphate solution $(Na_2S_2O_3.5H_2O)$ 0.1(N) Finally titrating with standard sodium thiosulfate solution $(Na_2S_2O_3)$ to a starch indicator end point to a starch indicator end point. The rate of sodium sulfite consumption was determined determine from titration of sodium sulphite against sodium thiosulphate and k_La calculated according to the following equation. $((-dC_{Na2SO3})/dt) = 2K_LaC^*$. The order of the reaction for both i.e., oxygen consumption and sodium sulphite consumption are determined by plotting ln (C/Co) versus time for oxygen consumption and concentration of sodium sulphite versus time for sulphite consumption to obtain linear plots [1].

Experimental design and data analysis: Central composite design (CCD)

In order to study the combined effect of design or mechanical parameters such as impeller speed, and process or chemical parameters such as air flow rate , a statistical approach namely response surface methodology has been used. The process conditions can be optimized using Response surface methodology. Response surface methodology is an empirical modelization technique devoted to the evaluation of the relationship of a set of controlled experimental factors and observed results. Basically this optimization process involves three major steps, performing the statistically designed experiments, estimating the coefficients in a mathematical model, and predicting the response and checking the adequacy of the model. The Central composite design is employed for the optimization of process conditions [7]. According to the Central composite design, the total number of treatment combinations was $2^k + 2k + n_o$ where 'k' is the number of independent variables and n_o is the number of repetition of experiments at the center point. The total number of design points is thus $N = 2^k + 2k + n_o$. The significant variables like speed of impeller & air flow rate were chosen as the critical variables and designated as X_1 and X2 respectively. The low, middle, and high levels of each variable were designated as −, 0, and + respectively. -α and +α are the extreme levels in the range studied for each variable ,α describe a circular design geometry ,which reduce errors by locating the axial points at the lower and upper bound of the variable ranges, which gives direct , mutual, curvilinear interaction . Factorial point should range -1 and +1, axial point −1.414 and +1.414 are intermediate levels between the central and extreme levels of each variable, and 0 is the central level in the range studied for each variable. The experimental range for Speed of impeller & Air flow rate are chosen for this study (Obtained using Design Expert Software, Stat-Ease, U.S.A.) is given in Table 1.

A 2^2-factorial central-composite-experimental-design was employed and all in duplicate, leading to 13 sets of experiments, was used to optimize the mass transfer coefficient. Experimental plan employed for the optimization of impeller speed and air flow rate. For statistical calculation, the variable Xi have been coded as xi according to the following transformation: $xi = (Xi - Xo)/\delta X$, Where xi is the dimensionless coded value of the independent variable Xi, Xo is the actual value of the independent variable Xi at the center point and X is the step change. The optimum mass transfer coefficient is taken as the dependent variable or response Ŷ. Regression analysis was performed on the data obtained. The behavior of the system was explained by the following second order polynomial equation. $Y = \beta o + \Sigma \beta i\ xi + \Sigma \beta ii\ xi^2 + \Sigma \beta ij\ xi\ xj$, where, Y = predicted response, βo = offset term, βi = linear effect, βii = squared effect, and βij = interaction effect. xi and xj = coded value of independent variables. The regression equation was optimized for maximum value to obtain the optimum conditions using MATLAB version 7.0 The second order polynomial equation was obtained using Design-Expert software [8].

Results and Discussions

The volumetric mass transfer coefficient was determined using sodium sulphite oxidation method. The experiments were carried out in 2 L (working volume) fermenter. The conventional practice of single factor optimization by keeping other involving factors at unspecified constant levels does not depict the combined effect of all the factors involved. Also this method requires carrying out a number of experiments to determine the optimum levels, which will not give true values. Optimizing all the affecting parameters combined by statistical experimental design can eliminate these drawbacks of single factor optimization process. The effect of the process conditions namely impeller speed and air flow rate were studied using a second order central composite experimental design (CCD) [7]. A total of 13 experiments with different combinations of impeller speed and air flow rate were performed using central composite design to find the parameter conditions where the optimum volumetric mass transfer coefficient occurs. Table 2 show the comparison between experimental and predicted values for the volumetric mass transfer coefficient using sodium sulphite oxidation method. The error was well within $\pm$ 10 % indicating that the empirical expression for the prediction of volumetric coefficient is valid. The expression obtained in terms of coded factors is given by the equation, $Y_1 = 607.58 - 23.99x_1 - 36.60x_2 - 15.08x_1x_2 + 27.66x_1^2 + 14.59x_2^2$, where Y_1 is the response variable i.e., volumetric mass transfer coefficient, x_1 and x_2 are coded values of independent variables, i.e., impeller speed and air flow rate respectively . Actual form of the empirical expression gives the predicted value of

volumetric mass transfer coefficient. $Y_2 = 749.257 - 0.5878X_1 - 4.3599X_2 - 0.02512X_1X_2 + 0.0006 X_1^2 + 1.618 X_2^2$. Where Y_2 is the response variable, Volumetric mass transfer coefficient. X_1 and X_2 actual values of independent variables, i.e., impeller speed and air flow rate respectively.

The independent and the dependent variables were fitted to the second-order model equation. They were examined in terms of the goodness of fit. The goodness of fit of the regression equation Y_1 was evaluated by the coefficient of determination (R^2) and the coefficient of relation (R). The coefficient of determination (R^2) is a measure of total variation of observed values of extracted oil about the mean explained by the fitted model. The coefficient of correlation (R) explains the correlation between the experimental and predicted values from the model. A good model equation explains most of the variations in the response. The coefficient of determination (R^2) is 0.9204. This value indicates that the response model can explain 92.04% of the total variability in the responses. The coefficient of correlation (R) is 0.9593.The closer value of coefficient of correlation (R) to unity is the better. Statistical testing of the model was done in the form of variance (ANOVA), which is required to test the significance and adequacy of the model. The reliability of the suggested model was tested using the Fisher's statistical test (F). The results of statistical testing using ANOVAs are given in Table 3.

Values of " Probability (P) > F"less than 0.05 indicate that the model terms are significant. The ANOVA of the regression model corresponding to quadratic for volumetric mass transfer coefficient Table 3 demonstrates that the model is highly significant, as it is evident from the calculated F-value (= 28.74) and a very low probability value (Probability(P) > F = 0.0009). Moreover the computed F-value (F= 28.74) is much greater than the F value ($F_{0.005 (5, 7)}$ = 9.52) obtained from the standard distribution table, so the null hypothesis is rejected at 5% α level of significance [7-8]. From Figure 1 it can be observed that a stationary point exists although it is outside the range based on the shape of the contour plot. The response surface plot shown in Figure 2 for the chosen model Y_1 illustrates the three dimensional relationship for the effects of impeller speed and air flow rate on volumetric mass transfer coefficient. The response surface indicates that the volumetric mass transfer coefficient increases with decrease in impeller speed and subsequent increase in air flow rate. This result indicates that two variables had mutually dependent influence on the volumetric mass transfer coefficient.

CONCLUSION

Evaluation of mass transfer coefficients in fermenters were studied using central composite design to get the optimum value. A total of 13 experiments for each set were employed to determine the volumetric mass transfer coefficients. The order of the reaction for oxygen consumption for 2 L sodium sulphite oxidation method was found to be first order and zero order for the case of sodium sulphite oxidation. Optimum volumetric mass transfer coefficient was found from response surface methodology to be outside the range of parameters studied. Analytical expressions for predicting the volumetric mass transfer coefficient for the range of impeller speed and air flow rate tested were obtained using response surface methodology.

Nomenclature

k_La = Volumetric mass transfer coefficient, C^* = Equilibrium concentration in moles /liter, t = Time in minutes or sec and C_{Na2S03} = Concentration of sodium sulphite in mol/liter

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Table 1. Experimental range and levels of impeller speed and air flow rate in Central composite design (CCD).

Parameter	Level				
	-α	-1	0	+1	+α
Speed of impeller	217.16	300	500	700	782.84
Air flow rate	4.76	6	9	12	13.24

Table 2. Comparison of experimental and predicted values of volumetric mass transfer coefficient for 2 L sodium sulphite oxidation method

Run	Impeller speed (rpm)	Air flow rate (lpm)	Volumetric mass transfer coefficient k_La (hr^{-1})		(%)-Error
			Experimental	Model	
1	500.00	9.00	611.985	608.583	0.555
2	782.84	9.00	609.151	675.977	1.177

| 3 | 217.16 | 9.00 | 710.677 | 675.977 | 0.588 |
4	500.00	9.00	609.151	608.583	0.093
5	500.00	9.00	607.735	608.583	-0.139
6	500.00	9.00	604.151	608.583	0.608
7	300.00	12.00	727.204	721.619	-0.768
8	500.00	13.24	670.539	678.583	-1.257
9	700.00	12.00	672.900	670.774	0.315
10	500.00	4.76	596.402	575.691	3.472
11	700.00	6.00	609.151	626.961	-2.923
12	500.00	9.00	604.902	608.583	0.093
13	300.00	6.00	603.151	608.583	-2.497

Table 3. Analysis of Variance (ANOVA) Table for the effect of

speed of impeller, air flow rate on volumetric mass transfer coefficient.

Source	Sum of squares	Degrees of freedom	Mean square	F value	*Probability(P)>F
Model	24505.94	5	4901.19	28.74	0.0009
Error	1193.78	7	170.54		significant
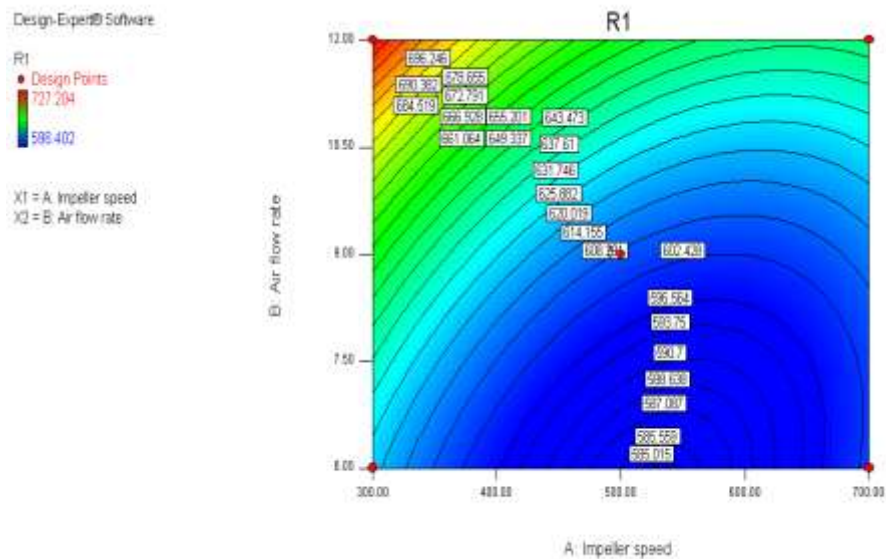
Figure 1. Isoresponse contour plots showing the effect of impeller speed and air flow rate and their interactive effect on the volumetric mass transfer coefficient for 2 L sodium sulphite oxidation method.
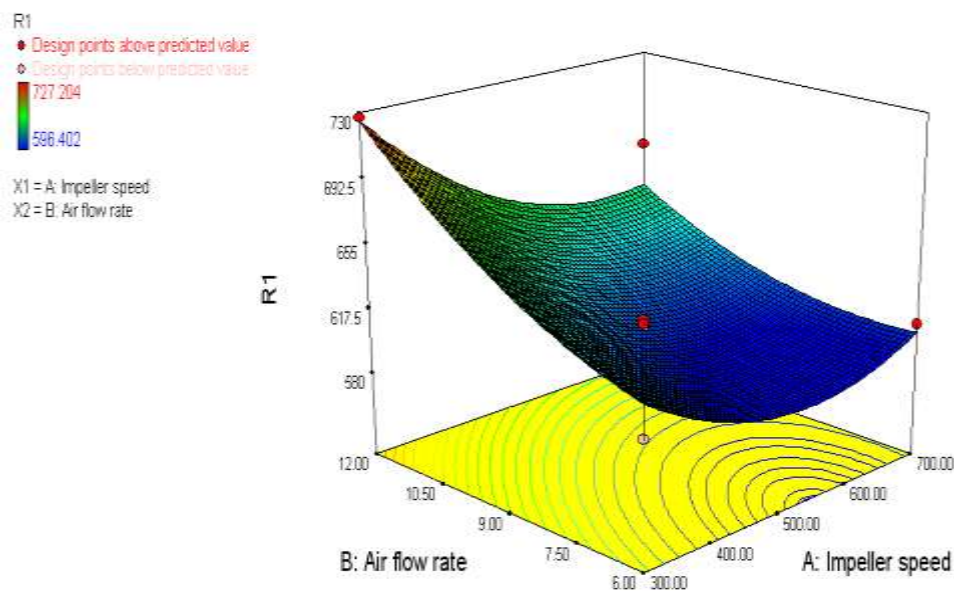
Figure 2. Response surface plot showing the effect of impeller speed and air flow rate and their interactive effect on the volumetric mass transfer coefficient for 2 L sodium sulphite oxidation method

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