

# Evaluation of the optical sulfite oxidation method for the determination of the interfacial mass transfer area in small-scale bioreactors

V. Linek\*, M. Kordač, T. Moucha

Department of Chemical Engineering Prague Institute of Chemical Technology 166 28 Prague 6, Czech Republic

Received 11 January 2005; received in revised form 11 July 2005; accepted 3 August 2005

## Abstract

The optical sulfite oxidation method was recently used by Hermann et al. [R. Hermann, M. Lehmann, J. Büchs, Characterization of gas–liquid mass transfer phenomena in microtiter plates, *Biotechnol. Bioeng.* 81 (2003) 178–186] and Kensy et al. [F. Kensy, H.F. Zimmermann, I. Knabben, T. Anderlei, H. Trauthwein, U. Dingerdissen, J. Büchs, Oxygen transfer phenomena in 48-well microtiter plates: determination by optical monitoring of sulfite oxidation and verification by real-time measurement during microbial growth, *Biotechnol. Bioeng.* 89 (2005) 698–708.] for determination of interfacial mass transfer area  $a$  in a microtiter plate at different shaking intensities. They have determined relative increase of a liquid surface area due to the shaking as a ratio of average specific oxygen absorption rates  $N_{\text{ave}}$  in 0.5 M sulfite solution with  $10^{-4}$  M  $\text{CoSO}_4$  under shaken and unshaken conditions. In this paper it is shown that the method is based on the assumption that the profiles of instantaneous oxygen flux  $\Phi$  during the whole experiments are the same for the shaken and nonshaken solutions. Our experiments performed in a stirred cell did not confirm validity of this assumption. Monitoring of pH and sulfite concentration during the oxidation of sulfite solutions revealed lower values of  $\Phi$  into nonagitated solution compared to agitated one. The value of  $N_{\text{ave}}$  in the nonagitated (nonshaken) sulfite solution was by 30% lower than the rate in the agitated one. Consequently, the mass transfer areas measured by the optical sulfite oxidation method are overestimated seriously, cca. 1.4 times. The lower oxygen transfer rate in the nonagitated solution is caused by a local drop of the sulfite concentration near the interface which is due to insufficiently fast transport of sulfite ions from the bulk of a liquid phase to interface under nonagitated (nonshaken) conditions. It is shown that the optical method for measuring of  $a$  is fundamentally flawed and should not be used in the presented form.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Bioreactors; Gas–liquid mass transfer; Oxygen transfer; Microtiter plates; Sulfite oxidation; Optical method

## 1. Introduction

Recently, Hermann et al. [1] presented a new optical method based on sulfite oxidation for measuring of volumetric mass transfer coefficient  $k_L a$ , specific mass transfer area  $a$  and mass transfer coefficient  $k_L$ . The method was used also by Kensy et al. [2]. This noninvasive optical method, easy-to-use in small-scale bioreactors such as microtiter plates, was originally developed by Hermann et al. [3] for measuring of the maximum oxygen transfer capacity  $\text{OTR}_{\text{max}}$  ( $=k_L a c^* = k_L a \text{He}(p_{\text{O}_2})_{\text{air}}$ ).

The optical method utilizes the fact that the sulfite is oxidized to the more acidic sulfate, which leads to a drop of pH at the end of the oxidation. The sharp pH-decrease to 6.2 is visualized by Bromothymol blue pH-indicator and it is used to measure the length of the sulfite oxidation reaction  $t_R$  which converts all of the sulfite to sulfate. Hermann et al. [1,3] calculated the specific oxygen transfer rate from the relation:

$$N_{\text{ave}} = \frac{C_{\text{Na}_2\text{SO}_3}}{\nu t_R} \quad (1)$$

$c_{\text{Na}_2\text{SO}_3}$  is the initial sulfite concentration and  $\nu=2$  is a sulfite stoichiometric coefficient in the reaction:  $2\text{Na}_2\text{SO}_3 + \text{O}_2 \rightarrow 2\text{Na}_2\text{SO}_4$ . The values of  $N_{\text{ave}}$  measured by the optical method are therefore the transfer rates averaged

\* Corresponding author. Tel.: +420 220 443 298; fax: +420 223 337 335.  
E-mail address: vaclav.linek@vscht.cz (V. Linek).

### Nomenclature

$A$	gas–liquid mass transfer area in the cell ( $\text{m}^2$ )
$a$	specific mass transfer area ( $1/\text{m}$ )
$c^*$	oxygen concentration in liquid at interface ( $\text{kmol}/\text{m}^3$ )
$c_{\text{Na}_2\text{SO}_3}$	sulfite concentration ( $\text{kmol}/\text{m}^3$ )
$D$	diffusion coefficient in liquid phase ( $\text{m}^2/\text{s}$ )
He	oxygen solubility ( $\text{kmol}/\text{m}^3/\text{Pa}$ )
$k_L$	physical liquid-side mass transfer coefficient ( $\text{m}/\text{s}$ )
$k_2$	second-order reaction constant ( $\text{m}^3/\text{kmol}/\text{s}$ )
$N_{\text{ave}}$	average specific oxygen transfer rate measured by the optical method ( $\text{kmol}/\text{m}^3/\text{s}$ )
OTR	oxygen transfer rate ( $\text{kmol}/\text{m}^3/\text{s}$ )
$p_{\text{O}_2}$	oxygen partial pressure (Pa)
$t_R$	reaction time (s)
$\Phi$	instantaneous oxygen flux ( $\text{kmol}/\text{m}^2/\text{s}$ )
$\nu$	sulfite stoichiometric coefficient
$\tau$	exposure time of surface elements (s)

over the whole measuring period. A relation between the reaction time  $t_R$  and the profile of instantaneous oxygen flux  $\Phi$  into the sulfite solution is given by:

$$t_R = \int_0^{c_{\text{Na}_2\text{SO}_3}} \frac{dc_{\text{Na}_2\text{SO}_3}}{\nu a \Phi} \quad (2)$$

Substitution of (2) into (1) gives the relation between the average specific oxygen transfer rates  $N_{\text{ave}}$  measured by the optical method and the profile of instantaneous oxygen flux  $\Phi$  in the experiment:

$$N_{\text{ave}} = \frac{c_{\text{Na}_2\text{SO}_3} a}{\int_0^{c_{\text{Na}_2\text{SO}_3}} (dc_{\text{Na}_2\text{SO}_3}/\Phi)} = \frac{0.5a}{\int_0^{0.5} (dc_{\text{Na}_2\text{SO}_3}/\Phi)} \quad (3)$$

If the oxygen flux  $\Phi$  is constant during all the experiment, Eq. (3) reduces to:

$$N_{\text{ave}} = a \Phi \quad (4)$$

For measuring of the maximum oxygen transfer capacity  $\text{OTR}_{\text{max}}$  Hermann et al. [3] used air absorption into 0.5 M sodium sulfite with addition of  $10^{-7}$  M  $\text{CoSO}_4$  as a catalyst, 0.012 M  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$  phosphate buffer (pH 8) and  $2.4 \times 10^{-5}$  M Bromothymol blue at temperature  $22^\circ\text{C}$ . Hermann et al. [3] adjusted the conditions (pH, buffer, and catalyst concentration) so as to obtain such reaction rate, which does not enhance the physical mass transfer and is sufficiently rapid to keep the oxygen concentration in the bulk of the liquid phase on negligibly low level. The oxygen absorption flux is then constant over the whole period of the sulfite oxidation reaction and equal to  $\Phi = k_L c^* = k_L \text{He}(p_{\text{O}_2})_{\text{air}}$ . Hermann et al. [3] verified this experimentally by monitoring the instantaneous oxygen transfer rate. From the Eq. (4) then follows that  $N_{\text{ave}} = k_L a c^* = \text{OTR}_{\text{max}}$ .

For measuring of the specific mass transfer area  $a$  Hermann et al. [1] used air absorption into the sulfite solution with addition of  $10^{-4}$  M  $\text{CoSO}_4$  (instead of  $10^{-7}$  M) as a catalyst. The authors assumed that the oxygen flux into the solution at high catalyst concentration is described by a model of absorption accompanied by a moderate second order irreversible reaction rate with respect to oxygen and zero order with respect to sulfite. Danckwerts [4] derived following relation for the oxygen flux under these specific conditions (moderately rate reaction, zero order in sulfite)

$$\Phi = (c^*)^{3/2} \sqrt{\frac{2}{3} D_{\text{O}_2} k_2} \quad (5)$$

The expression “moderate reaction rate” means that all oxygen entering the liquid phase reacts completely within the liquid film. Hydrodynamic conditions prevailing in the liquid have no influence on the oxygen flux under given conditions (moderately rate reaction, zero order in sulfite). Hermann et al. [1] assumed that Eq. (5) holds over all the oxidation reaction of sulfite to sulfate and used following relation for interpretation of their experiments:

$$N_{\text{ave}} = a(c^*)^{3/2} \sqrt{\frac{2}{3} D_{\text{O}_2} k_2} \quad (6)$$

with knowledge of the oxygen solubility ( $c^*$ ), the oxygen diffusivity ( $D_{\text{O}_2}$ ) and the kinetic constant of the reaction ( $k_2$ ) the specific mass transfer area ( $a$ ) can be calculated from the measured value of  $N_{\text{ave}}$ . It is not recommended to take the rate constant of the reaction from the literature because of the large number of substances that can interfere with the reaction. Hermann et al. [1] therefore predetermined the value of  $k_2$  for the applied sulfite solution from the oxygen transfer rate  $N_{\text{ave,nonagit}}$  measured in the microtiter plate by the experiment performed under nonshaken conditions. (As the nonshaken and shaken conditions correspond with the nonagitated and agitated conditions respectively, the latter notification (agit, nonagit) is used in subscripts.) Under these conditions the specific mass transfer area  $a_{\text{nonagit}}$  is known and equals to the ratio of the cross-section area of the microtiter plate to a liquid filling volume. Hermann et al. [1] calculated the value of the specific mass transfer area  $a_{\text{agit}}$  for different operating conditions in the shaken microtiter plate (stirring frequency, shaking diameter, filling volume) from following equation, which results from the Eqs. (6):

$$a_{\text{agit}} = a_{\text{nonagit}} \frac{N_{\text{ave,agit}}}{N_{\text{ave,nonagit}}} \quad (7)$$

$N_{\text{ave,nonagit}}$  and  $N_{\text{ave,agit}}$  were measured using the same sulfite solution (concentration of sulfite, cobalt catalyst, pH, temperature, oxygen pressure).

Eq. (5) was derived for the oxygen flux under specific conditions, which are not fulfilled over the whole period of the sulfite oxidation reaction. Specifically, Linek [5] and Linek and Mayrhoferová [6] determined that the reaction is of zero order when the sulfite concentration is higher than 0.2 M.

Download English Version:

<https://daneshyari.com/en/article/5083>

Download Persian Version:

<https://daneshyari.com/article/5083>

[Daneshyari.com](https://daneshyari.com)