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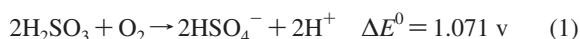
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The aim of this work was to study the effect of the initial sulfite concentration on the stoichiometric coefficient of sulfite oxidation. A combined method based on the oxidation of sulfite by oxygen in the presence of cobalt(II) (0.5 mM) as catalyst was used to determine the volumetric mass transfer coefficient (k_La) and the oxygen consumption (OC) due to sulfite oxidation. Results demonstrated that the dissolved oxygen (DO) probe response constant (k_{sensor}) was not dependent on the DO concentration or the agitation speed; obtained k_{sensor} values were high enough to not interfere with DO or OC measurements. Using the reaction time to sulfite depletion method, volumetric mass transfer coefficient (k_La) yielded a linear increase as a function of the initial sulfite concentration. On the contrary, from the saturation phase of DO curves, an almost constant k_La value was obtained in accordance to constant air flow rate and agitation conditions that were used in the experiments. The observed stoichiometric coefficient (OC/S_0) at high initial sulfite concentrations or low k_La values was lower than the theoretical one, suggesting that the formation of elemental sulfur becomes significant at these conditions.

1. Introduction

Gaseous sulfur dioxide (SO_2) is highly soluble in water, forming hydrated sulfur dioxide ($SO_2(aq)$), bisulfite (HSO_3^-), sulfite (SO_3^{2-}), and, at high concentrations, disulfite ($S_2O_5^{2-}$). The term S(IV) includes all compounds containing sulfur in the oxidation state 4+, such as the above-mentioned species. Sulfur(IV) oxides are ubiquitous in the environment. The combustion of fossil fuels is the main source of sulfur dioxide.[1] In addition, sulfites are widely used as preservatives in food, wine, and drugs. In response to EPA regulations, the pulp and paper industry developed mechanical pulping processes that use sulfite instead of chlorine to avoid dioxin problems.[2] Other industrial usages of sulfur(IV) compounds include the removal of hexavalent chromium from industrial wastewaters, with gaseous sulfur dioxide and sodium sulfite being the most commonly used reducing agents.[3]

In all cases, the excess of sulfite must be oxidized using forced oxidation for example, to avoid contamination problems. Sulfite oxidation by oxygen in aqueous solutions is strongly favorable at both acidic and alkaline conditions, the overall reactions are the following:[4]

$$2H_2SO_3 + O_2 \rightarrow 2HSO_4^- + 2H^+ \quad \Delta E^0 = 1.071 \text{ v} \quad (1)$$

$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-} \quad \Delta E^0 = 1.337 \text{ v} \quad (2)$$

Catalytic oxidation of sulfite by oxygen was extensively studied. It has been shown that trace amounts of catalysts such as $Fe^{2+/3+}$, Co^{2+}, Cu^{2+}, and Mn^{2+} strongly affect the reaction rate.[5] Ogawa et al.[6] showed that, for sulfite concentrations above its critical value, the reaction rate is second order with respect to dissolved oxygen, first order with respect to the catalyst concentration (Co^{2+}), and zero order with respect to sulfite. Barron and O'Hern[7] studied the reaction catalyzed by copper; those authors reported 3/2 kinetic order in total sulfite and zero order in oxygen. Bengtsson and Bjerle[8] studied the reaction

catalyzed by cobalt; they reported the rate as zero order in oxygen, 3/2 in sulfite, and 1/2 in cobalt.

Sulfite oxidation by dissolved oxygen takes place through complex chain reactions involving several sulfur containing radicals such as $\dot{S}O_3^-$, $\dot{S}O_4^-$, and $\dot{S}O_5^-$.[9] In addition, the formation of other radicals such as SO_2^- and $\dot{O}H$ has been reported also;[10,11] all these radicals may react, yielding parallel reactions and with one another to form inactive compounds. It must be pointed out that different metals are usually found in industrial wastewaters; thus, a high catalyst concentration is frequently achieved. Because the total amount of radicals also depends on the catalysts concentrations, the overall stoichiometry is strongly dependent on the experimental conditions. Although the reaction kinetics of sulfite with oxygen was extensively studied, little attention has been focused on its stoichiometry. The knowledge of the actual stoichiometry of sulfite oxidation by oxygen is useful to optimize aeration and power input of sulfite-removing processes, for example. For these reasons, the aim of this work was to study the stoichiometry of the reaction between sulfite and oxygen in an aerated stirred-tank reactor using a high catalyst concentration.

2. Materials and Methods

2.1. Experimental Setup. Sulfite oxidation experiments were performed in a cylindrical reactor of 6 cm in internal diameter and 23 cm in total height with a working volume of 500 mL. The temperature (25 ± 0.5 °C) was controlled by means of a water bath. The reactor was agitated by a magnetic stir bar with variable agitation speed (4–8, arbitrary units). The aeration was supplied from an air pump; air flow rate was controlled using a high-precision rotameter (Bruno Schilling model MB 60V, Argentina). The air passed through a humidifier and then entered the bottom of the reactor. The air sparger consisted of a diffuser, which formed coarse bubbles. Dissolved oxygen (DO) was continuously measured with a polarographic DO probe (YSI model 5739) with a standard membrane (YSI) connected to a DO monitor (YSI model 58); data were acquired with a computer interfaced to the DO monitor at 1 data/s.

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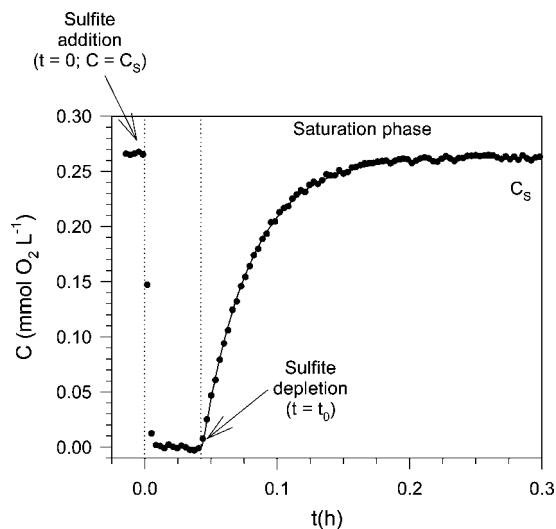
Figure 1. Typical example of the dissolved oxygen (C) as a function of time due to the addition of sodium sulfite (75 mg). For the sake of clarity, only 1 out of 10 data points were plotted. Dotted lines represent $t = 0$ and $t = t_0$; the continuous line represents eq 6.

2.2. Chemicals. Pure cobalt(II) chloride-6-hydrate ($>99\%$) was obtained from Sigma (St. Louis, MO). Analytical-grade sodium sulfite ($>99\%$) was from Anedra (San Fernando, Argentina). Deionized water was used in all the experiments.

2.3. Dissolved Oxygen Probe Response Constant. The time constant of the oxygen sensor was determined before each set of experiments. The DO sensor was placed in a beaker of water saturated with oxygen; then, at $t = 0$, the sensor was inserted in the reactor filled with a solution of DO concentration (C_F) lower than the saturation concentration (C_S). This solution was obtained by the addition of an excess of sodium sulfite to remove all the DO, and then the solution was aerated until the desired DO concentration (C_F) was reached; tested C_F values ranged from 0.03 to 0.24 (mmol of O_2) L^{-1}. Because a typical experiment lasted about 1 min, C_F was almost constant. In this condition, the first-order DO probe-response constant (k_{sensor}) was calculated by fitting the following expression to the measured DO concentration (C) as a function of time (t),[12]

$$C = C_F + (C_S - C_F) e^{-k_{sensor}t} \tag{3}$$

where C_S and C_F are the saturation and final DO concentrations, respectively.

2.4. Determination of Volumetric Mass Transfer Coefficient (k_La) and Oxygen Consumption (OC). A combined method based on the oxidation of sulfite by oxygen in the presence of cobalt(II) as catalyst was used to determine the volumetric mass transfer coefficient (k_La) of the reactor and the oxygen consumption during the sulfite oxidation. Although Puskeiler and Weuster-Botz[13] suggest 1 mmol L^{-1} for the catalyst, a lower concentration was employed (0.5 mmol L^{-1}) to avoid the formation of $Na_2(Co(SO_4)_2)$ precipitated during the assays.[14] The reactor was continuously aerated to achieve a DO saturation concentration ($C = C_S$). Then, at $t = 0$, known amounts of sodium sulfite were added to remove the oxygen from the reactor and the DO concentration dropped to about zero (C_0). After the sulfite depletion at $t = t_0$, the DO concentration increased to reach its saturation concentration (C_S) (Figure 1). The oxygen mass balance in the reactor is

$$\frac{dC}{dt} = k_La(C_S - C) - R \tag{4}$$

where R is the observed oxygen consumption rate. From Figure 1, it is clear that, during the sulfite oxidation ($0 < t < t_0$), the
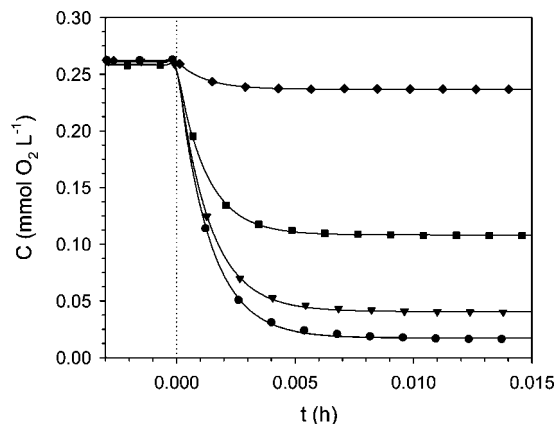

Figure 2. DO probe response to different step changes in the DO concentration. Lines indicate the results obtained by fitting eq 3 to the experimental data.

DO concentration is negligible ($C \approx 0$). In this condition, integration of eq 4 yields the following[13]

$$k_La = \frac{OC - C_S}{C_S t_0} \tag{5}$$

where $OC = \int_0^{t_0} R \, dt$ is the oxygen consumed during the sulfite oxidation. If the initial sulfite concentration is known, then OC can be estimated from the stoichiometry of the sulfite oxidation ($OC_{st} = 0.5$ mol of oxygen consumed per mol of sulfite oxidized).

In order to determine the actual OC value, k_La also was calculated from the saturation phase ($t > t_0$, Figure 1). In this case, if the first part of the DO profile is discarded (the fast drop of DO), and taking into account the finite response time of the DO probe, the measured DO concentration (C) as a function of time is[12]

$$C =$$
$$\begin{cases} C_0 & t < t_0 \\ C_S + \dfrac{(C_0 - C_S)}{k_{sensor} - k_La}[k_{sensor} \, e^{-k_La(t-t_0)} - k_La \, e^{-k_{sensor}(t-t_0)}] & t \geq t_0 \end{cases} \tag{6}$$

where k_{sensor} is the DO probe-response constant. Once k_La value was obtained, the oxygen consumption (OC) during the sulfite oxidation was calculated using the following expression[15]

$$OC = k_La \int_0^t (C_S - C) \, dt - C + C_S \tag{7}$$

In the present paper, the software Sigma Plot 9.0 was used for all the nonlinear fittings. An algorithm based on the trapezoidal rule was implemented in Sigma Plot 9.0 in order to evaluate the integral in eq 7 from the experimental data.

3. Results and Discussion

3.1. Dissolved Oxygen Probe-Response Constant. The DO probe-response constant (k_{sensor}) was determined in order to verify if its effect on the DO measurements was significant. Figure 2 shows some examples of the DO probe response to different step changes in the DO concentration; for the sake of clarity, only one out of five data points was plotted. All curves follow the used first-order model; thus, eq 3 was fitted to the data in order to calculate the DO probe-response constant (k_{sensor}). Figure 3 shows that k_{sensor} was not dependent on the final DO concentration or the agitation (Table 1). Obtained values for k_{sensor} ranged between 691 and 918 h^{-1}; the overall mean k_{sensor} was 814 ± 18 h^{-1}. This result is close to those
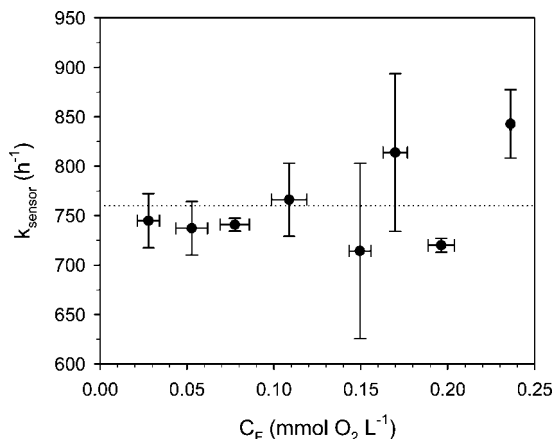
Figure 3. Effect of the final DO concentration (C_F) on the DO probe response constant (k_{sensor}). Bars indicate the 95% confidence interval. The dotted line indicates the overall mean value for k_{sensor}.

Table 1. Effect of the Agitation on the DO Probe-Response Constant (k_{sensor})

agitation (arbitrary units)	k_{sensor} (h^{-1})
4	896 ± 18
5	886 ± 15
6	882 ± 11
7	900 ± 18
8	882 ± 18

reported by other authors. For example, Vandu and Krishna[16] studied the time response of a polarographic DO sensor (YSI model 5331), a very similar one to that used in the present paper; those authors reported DO probe-response constants that ranged from 1440 to 1650 h^{-1}. Philichi and Stentrom[17] reported k_{sensor} values of 900 and 468 h^{-1} for high sensivity and normal membranes, respectively.

3.2. Effect of Initial Sulfite Concentration on the Determination of Volumetric Mass Transfer Coefficient (k_La). The volumetric mass transfer coefficient (k_La) of the reactor was determined using the combined sulfite method proposed by Puskeiler and Weuster-Botz[13]. Tested initial sulfite concentration ranged from 0.6 to 6.4 (mmol of sulfite) L^{-1}; in all cases, k_La values were determined using both eqs 5 and 6 at a constant air flow rate (0.5 L min^{-1}) and agitation (7, expressed in arbitrary units). Figure 4 shows that the reaction time (the time to sulfite depletion) increased with the initial sulfite concentration; from this phase, eq 5 was used to determine k_La
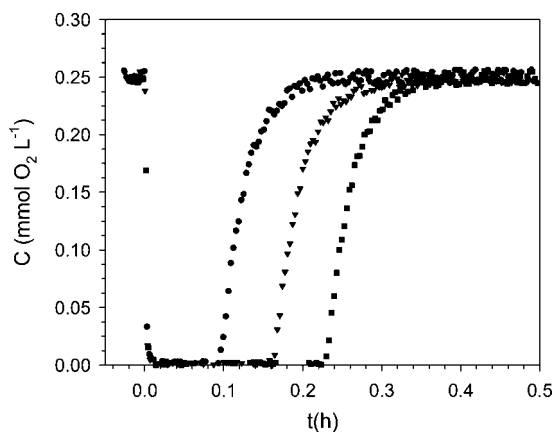

Figure 4. Dissolved oxygen concentration (C) as a function of time corresponding to the following initial sulfite concentrations: (●) 2.4 mmol L^{-1}, (▼) 3.9 mmol L^{-1}, and (□) 6.3 mmol L^{-1}.
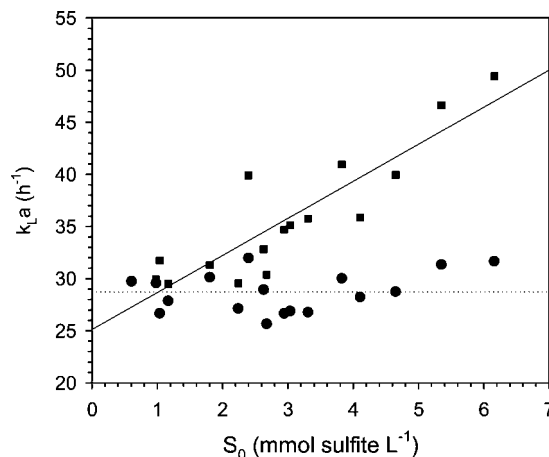

Figure 5. Effect of the initial sulfite concentration (S_0) on the calculated volumetric mass transfer coefficient (k_La) using eq 5 (squares) and eq 6 (circles). The continuous line represents the trend of obtained k_La by means of eq 5; the dotted line represents the overall mean $k_La = 28.8 \pm 0.9$ h^{-1} using eq 6.

based on the reaction time (t_0). Besides, from the saturation phase corresponding to each curve, k_La values were calculated by means of eq 6. Figure 5 shows that eq 5 yielded a linear increase of k_La as a function of the initial sulfite concentration. On the contrary, an almost constant k_La value was obtained with eq 6; in this case, the overall mean k_La was 28.8 ± 0.9 h^{-1}. In addition, similar k_La values were obtained using both eqs 5 and 6 at low initial sulfite concentrations. It must be pointed out that obtained k_La values were about 28 times lower than the DO probe-response constant (k_{sensor}). Philichi and Stentrom[17] demonstrated that, depending on both the calculation procedure and the precision needed, the effect of the response time of the DO probe on the k_La estimation can be neglected if the ratio k_{sensor}/k_La is higher than 20 to 50; this was the case in the present paper.

3.3. Effect of Initial Sulfite Concentration on the Actual Stoichiometry of Sulfite Oxidation by Oxygen (OC/S_0). Obtained k_La values using eq 6 were in accordance with conditions of constant air flow rate and agitation conditions that were used in the present experiments; this suggests that eq 5 overestimates k_La values at high initial sulfite concentrations, at least. It must be pointed out that eq 5 can be applied only if the assumed stoichiometry of the reaction between oxygen and sulfite is equal to the actual one. However, if parallel sulfite reactions occur, then the actual oxygen consumption (OC) may differ from the theoretical one based on the assumed stoichiometry ($OC_{st} = 0.5$ mmol of oxygen consumed per mmol of sulfite oxidized). Because obtained k_La values using eq 5 were higher than those calculated with eq 6, this suggests that OC_{st} were higher than the corresponding OC values. Therefore, for each tested initial sulfite concentration, eq 7 was used to calculate the actual OC. Figure 6 shows that, at low initial sulfite concentrations, both OC and OC_{st} (dotted line) are similar; however, at higher sulfite concentrations, OC_{st} overestimate the actual ones.

Within the tested initial sulfite concentrations, OC values as a function of the initial sulfite concentration (S_0) followed a second-order linear regression:
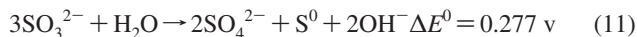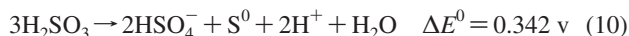
$$OC = aS_0 + bS_0^2 \qquad (8)$$

The regression results were the following: $a = 0.5$ (mmol of O_2)/(mmol of sulfite), $b = -0.03$ (mmol of O_2) L/(mmol of sulfite)^2 ($r^2 = 0.9959$). The actual stoichiometric coefficient can be obtained by rearranging eq 8:

$$OC/S_0 = a + bS_0 \qquad (9)$$

Figure 7 shows that, at low initial sulfite concentrations, the stoichiometry was similar to the theoretical one because coefficient a in eqs 8 and 9 was 0.5. However, within the tested experimental conditions, the actual OC at higher initial sulfite concentrations was lower than the calculated one using the theoretical stoichiometry (OC_{st}) because coefficient b was negative.

The difference between OC and OC_{st} (Figure 6) indicates that the amount of sulfite not oxidized by oxygen within the tested condition increases with the initial sulfite concentration. It must be pointed out that, when high initial sulfite concentrations were tested, a yellow/white precipitate was formed during the assays. This precipitate could be elemental sulfur that was produced through the following overall reactions:[4]
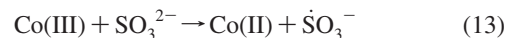
$$3H_2SO_3 \rightarrow 2HSO_4^- + S^0 + 2H^+ + H_2O \quad \Delta E^0 = 0.342 \text{ v} \quad (10)$$

$$3SO_3^{2-} + H_2O \rightarrow 2SO_4^{2-} + S^0 + 2OH^- \Delta E^0 = 0.277 \text{ v} \quad (11)$$

These ΔE^0 values indicate that, although sulfite oxidation by oxygen is more favorable (eqs 1 and 2), its disproportionation to sulfate and elemental sulfur is thermodynamically possible at both acidic and alkaline conditions. Reactions 10 or 11 could proceed as a two-step process. The first step involves sulfite
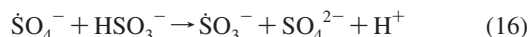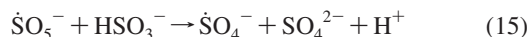

Figure 6. Oxygen consumption (OC) as a function of the initial sulfite concentration (S_0). The dotted line indicates the theoretical stoichiometry (OC_{st}). The continuous line represents the second-order linear regression (eq 8).

Figure 7. Effect of the initial sulfite concentration (S_0) on the observed stoichiometry (OC/S_0). The line indicates the calculated stoichiometry based on eq 9.

disproportionation to sulfate and sulfide; then, sulfide reacts with the excess of sulfite to form elemental sulfur.[18,19]

The most accepted reaction mechanism for sulfite oxidation by dissolved oxygen involves the following reactions:[9]

Initiation:

$$2Co(II) + O_2 + 2H^+ \rightarrow 2Co(III) + H_2O_2 \qquad (12)$$

$$Co(III) + SO_3^{2-} \rightarrow Co(II) + \dot{S}O_3^- \qquad (13)$$

Propagation:

$$\dot{S}O_3^- + O_2 \rightarrow \dot{S}O_5^- \qquad (14)$$

$$\dot{S}O_5^- + HSO_3^- \rightarrow \dot{S}O_4^- + SO_4^{2-} + H^+ \qquad (15)$$

$$\dot{S}O_4^- + HSO_3^- \rightarrow \dot{S}O_3^- + SO_4^{2-} + H^+ \qquad (16)$$

Termination:

$$R1 + R2 \rightarrow \text{inactive products} \qquad (17)$$

where R1 and R2 are any two free radicals. Once the $\dot{S}O_3^-$ radical is formed, it reacts with oxygen to sustain the chain reaction via eqs 14−16. If the oxygen mass transport rate is slower than its reaction rate, then DO concentration eventually drops to very low values and the rate of the first reaction of propagation (eq 14) decreases; in these conditions, sulfite disproportionation to sulfate and elemental sulfur through reactions 10 or 11 could occur. This effect can explain the difference between OC and OC_{st} depicted in Figure 6.

3.4. Effect of k_La (Agitation and Air Flow Conditions) on the Stoichiometry of Sulfite Oxidation. The above-mentioned experiments demonstrated that, when agitation and air flow conditions were constant, the stoichiometric coefficient of the sulfite oxidation by oxygen decreased as the initial sulfite concentration increased. This effect could reflect parallel sulfite reactions (e.g., eqs 10 or 11) that may occur under the low DO conditions obtained during the oxidation of sulfite. As the initial sulfite concentration increased, the elapsed time under low DO conditions and, therefore, the effect of these parallel reactions on the stoichiometric coefficient also increased.

Another way to study the effect of low DO conditions on the sulfite oxidation stoichiometry is by changing the volumetric mass transfer coefficient (k_La). Thus, experiments were performed to study the effect of k_La on the stoichiometric coefficient of the sulfite oxidation by oxygen (OC/S_0). To obtain different k_La values, the agitation speed was varied between 4 and 7 (in arbitrary units) and air flow rate was varied from 0.2 to 1.0 L min^{-1}; under these conditions, k_La values obtained by eq 6 ranged from 1 to 34 h^{-1}. In all cases, the initial sulfite concentration tested was 4 mM. Figure 8 shows that the ratio OC/S_0 increased from 0.27 to 0.42 (mmol of O_2)/(mmol of sulfite) as k_La increased from 1 to about ∼10 h^{-1}; however, for k_La values higher than 10 h^{-1}, the ratio OC/S_0 was almost constant. It must be pointed out that the experiments described in the previous section (effect of S_0 on the stoichiometry of sulfite oxidation) were performed under these conditions because k_La values were about 30 h^{-1}. Obtained results indicate that the stoichiometric coefficient of the sulfite oxidation by oxygen (OC/S_0) depends on k_La and the initial sulfite concentration (S_0). A low DO concentration for a longer time can be obtained by both increasing the initial sulfite concentration and decreasing k_La. In both cases, OC/S_0 ratios lower than the theoretical one ($OC/S_0 = 0.5$) were obtained due to the effect of parallel reactions such as reactions 10 or 11.

The experiments performed in the present paper were conducted using a high catalyst concentration (0.5 mM), initial
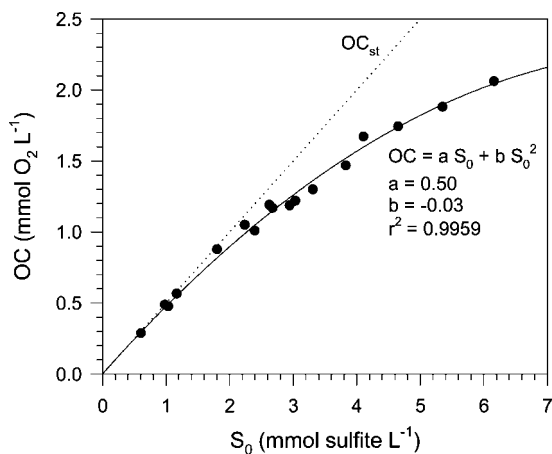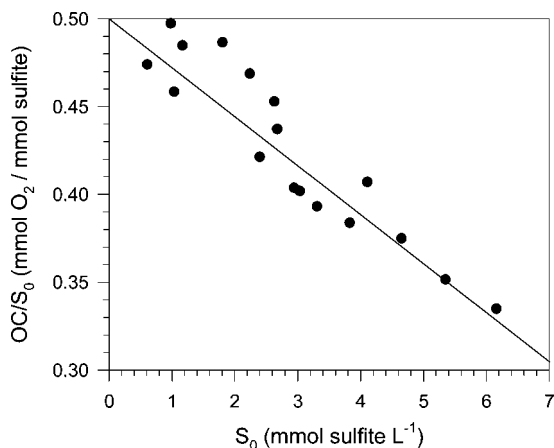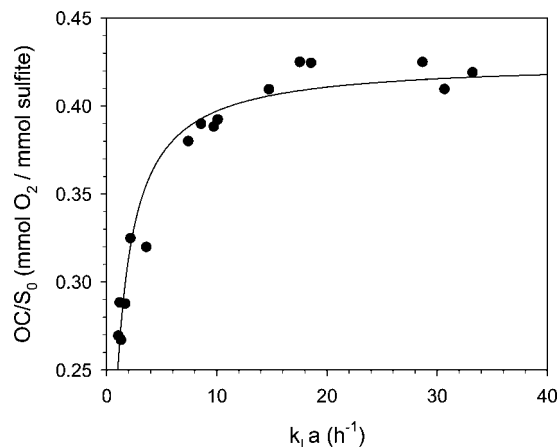
Figure 8. Effect of the volumetric mass transfer coefficient (k_La) on the observed stoichiometry (OC/S_0). The continuous line represents the trend of OC/S_0.

sulfite concentrations that ranged from 0.6 to 6.4 mM, and k_La values lower than 34 h^{-1}. Depending on the tested conditions, the dissolved oxygen concentration was close to zero up to 3 h. On the contrary, Puskeiler and Weuster-Botz[13] studied the oxidation of sulfite by oxygen using k_La values much higher (100−2000 h^{-1}) than that used in the present paper; therefore, the reaction time for sulfite oxidation determined by those authors ranged from 10 to 60 s. Although within this time the DO was close to zero, this reaction time was much shorter than those obtained in the present paper (up to 3 h). For this reason, sulfite disproportion to sulfate and elemental sulfur was negligible and those authors found that the reaction time was a linear function of the initial sulfite concentration.

Besides Co(II), other metals can serve as catalysts such as Cu(II) or Mn(II); therefore, high catalyst concentration conditions can be easily achieved, especially in industrial wastewaters. For example, gaseous sulfur dioxide and sodium sulfite are the most commonly used reducing agents for removing Cr(VI) from industrial wastewaters.[3] Beukes et al.[20] showed that a large excess of sulfite is needed to reduce Cr(VI) effectively in wastewaters. As a result, removal of residual sulfite from the treated wastewater (e.g., using aeration) is necessary to avoid contamination of receiving body waters. For a given residual sulfite concentration (S_0), the theoretical oxygen consumption is OC$_{st}$ = S_0/2. However, on the basis of the observed stoichiometry (OC/S_0) obtained in the present paper, the actual OC is lower than the theoretical one. For example, if S_0 = 6 mmol L^{-1}, the actual OC value calculated using eq 8 is 1.92 (mmol of O$_2$) L^{-1}, which represents a savings of 36% in the oxygen requirements.

4. Conclusions

In this work, the stoichiometry of the reaction between sulfite and oxygen in an aerated stirred-tank reactor using a high catalyst concentration was studied. Known amounts of sulfite were added to the reactor, and dissolved oxygen (DO) was monitored as a function of time.

Results demonstrated that the DO probe-response constant (k_{sensor}) was not dependent on the DO concentration or the agitation speed. The reaction time to sulfite depletion (eq 5) and the saturation phase of the DO as a function of time (eq 6) were used to determine the volumetric mass transfer coefficient (k_La) of the reactor. Results showed that eq 5 yielded a linear increase of k_La as a function of the initial sulfite concentration.

On the contrary, an almost constant k_La value = 28.8 ± 0.9 h^{-1} was obtained with eq 6, in accordance to constant air flow rate and agitation conditions that were used in the experiments. On the basis of this k_La value, the effect of the response time of the DO probe on the k_La estimation could be neglected because the ratio k_{sensor}/k_La was higher than 20.

Oxygen consumption (OC) measurements showed that actual and stoichiometric OC values at low initial sulfite concentrations (S_0) were similar; however, at higher sulfite concentrations, OC$_{st}$ overestimated the actual ones. Therefore, the observed stoichiometric coefficient (OC/S_0) at high initial sulfite concentrations was lower than the calculated one using the theoretical stoichiometry. The difference between the actual OC and OC$_{st}$ suggested that the formation of elemental sulfur becomes significant at high initial sulfite concentrations and low k_La values. Within the tested conditions, a reduction of 36% in the oxygen consumption was obtained.

Nomenclature

C = dissolved oxygen concentration ((mmol of O$_2$) L^{-1})
C_F = final dissolved oxygen concentration ((mmol of O$_2$) L^{-1})
C_S = saturation dissolved oxygen concentration ((mmol of O$_2$) L^{-1})
C_0 = initial dissolved oxygen concentration ((mmol of O$_2$) L^{-1})
DO = dissolved oxygen
k_La = volumetric mass transfer coefficient (h^{-1})
k_{sensor} = dissolved oxygen probe response constant (h^{-1})
OC = oxygen consumed during the sulfite oxidation ((mmol of O$_2$) L^{-1})
R = oxygen consumption rate ((mmol of O$_2$) L^{-1} h^{-1})
S_0 = initial sulfite concentration ((mmol of sulfite) L^{-1})
t = time (h)
t_0 = elapsed time until sulfite depletion (h)

Literature Cited

(1) Altshuller, A. P.; Linthurst, R. A. The acidic deposition phenomenon and its effects. *Critical Assessment Review papers*, Public review draft; EPA-600/8-83-016A; EPA: Washington, DC, 1983.

(2) McGhee-Lenart, R.; Hamann, J.; Morris, K.; Snyder, G.; Grossman, E.; Haller, J. *Effectiveness of Effluent Guidelines Program for Reducing Pollutant Discharges Uncertain*; EPA Report No. 2004-P-00025; EPA: Washington, DC, 2004.

(3) Conner, J. R. Fixation of metals. In *Chemical fixation of hazardous waste*; Conner, J. R., Ed.; Van Nostrand Reinhold: New York, 1990.

(4) Schriver, D. F., Atkins, P., Langford, C. H., Eds. *Inorganic Chemistry*, 2nd ed.; Freeman: New York, 1994.

(5) Berglund, J.; Fronaeus, S.; Elding, L. I. Kinetics and mechanism for manganese-catalyzed oxidation of sulfur(IV) by oxygen in aqueous solution. *Inorg. Chem.* **1993**, *32*, 4527.

(6) Ogawa, S.; Shimizu, Y.; Tone, S.; Otake, T. Kinetics of the oxidation of aqueous sodium sulfite solutions with air. *J. Chem. Eng. Jpn.* **1982**, *15*, 400.

(7) Barron, C.; O'Hern, H. A. Reaction kinetics of sodium sulfite oxidation by the rapid-mixing method. *Chem. Eng. Sci.* **1966**, *21*, 397.

(8) Bengtsson, S.; Bjerle, J. The absorption of oxygen into sodium sulfite solutions in a packed column. *Chem. Eng. Sci.* **1975**, *30*, 1429.

(9) Lancia, A.; Musmarra, D.; Pepe, F.; Prisciandaro, M. Model of oxygen absorption into calcium sulfite solutions. *Chem. Eng. J.* **1997**, *66*, 123.

(10) Mottley, C.; Mason, R. P.; Chignel, C. F.; Sivarajah, K.; Eling, T. E. The formation of sulfur trioxide radical anion during the prostaglandin hydroperoxidase-catalyzed oxidation of bisulfite (hydrated sulfur dioxide). *J. Biol. Chem.* **1982**, *257*, 5050.

(11) Netta, P.; Huie, R. E. Free-radical chemistry of sulfite. *Environ. Health Perspect.* **1985**, *64*, 209.

(12) Vandu, C. O.; Koop, K.; Krishna, R. Volumetric mass transfer coefficient in a slurry bubble column operating in the heterogeneous flow regime. *Chem. Eng. Sci.* **2004**, *59*, 5417.

(13) Puskeiler, R.; Weuster-Botz, D. Combined sulfite method for the measurement of the oxygen transfer coefficient k_La in bioreactors. *J. Biotechnol.* **2005**, *120*, 430.

(14) Zhao, B.; Li, Y.; Tong, H.; Zhuo, Y.; Zhang, L.; Shi, J.; Chen, C. Study on the reaction rate of sulfite oxidation with cobalt ion as catalyst. *Chem. Eng. Sci.* **2005**, *60*, 863.

(15) Vanrolleghem, P. A.; Kong, Z.; Rombouts, G.; Verstraete, W. An on-line respirographic biosensor for the characterization of load and toxicity of wastewaters. *J. Chem. Tech. Biotechnol.* **1994**, *59*, 321.

(16) Vandu, C. O.; Krishna, R. Influence of scale on the volumetric mass transfer coefficients in bubble columns. *Chem. Eng. Process.* **2004**, *43*, 575.

(17) Philichi, T. L.; Stenstrom, M. K. Effects of dissolved oxygen probe lag on oxygen transfer parameter estimation. *J. Water Pollut. Control Fed.* **1989**, *61*, 83.

(18) Habicht, K. S.; Canfield, D. E.; Rethmeier, J. Sulfur isotope fractionation during bacterial reduction and disproportionation of thiosulfate and sulfite. *Geochim. Cosmochim. Acta* **1998**, *62*, 2585.

(19) Wang, H.; Dalla Lana, I. G.; Chuang, K. T. Kinetics of reaction between hydrogen sulfide and sulfur dioxide in sulfuric acid solutions. *Ind. Eng. Chem. Res.* **2002**, *41*, 4707.

(20) Beukes, J. P.; Pienaar, J. J.; Lachmann, G.; Giesekke, E. W. The reduction of hexavalent chromium by sulphite in wastewater. *Water SA* **1999**, *25*, 363.