Gas absorption with zero-order chemical reaction in a foam-bed reactor

Amit Varshney, Piyush Agrawal, Ashok N. Bhaskarwar*

Department of Chemical Engineering, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India

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Abstract

A mathematical model for oxidation of aqueous alkaline solution of sodium dithionite using air as an oxidizing medium in a foam-bed reactor has been developed under pseudo-zero-order conditions of reaction and was found to be in good agreement with the experiments. Reactor conditions were 30°C at atmospheric pressure and surfactant used in the foam contactor was octyl phenoxy polyethoxyethanol (Triton X-100). The results of simulation for concentration profiles of the dissolved gas-phase reactant inside foam film based on above model are presented for different gas flow rates, reaction rates, and times of contact. The effects of variables such as superficial gas velocity and initial liquid-phase reactant concentration on conversion are also studied and compared with experiments on oxidation of sodium dithionite. The results indicate that the conversion increases with the increase in the superficial air velocity and initial dithionite concentration. The model predicts the experimentally obtained conversions reasonably well.

Keywords: Absorption; Zero-order reaction; Foam; Mathematical model; Experimental data; Oxidation of dithionite

1. Introduction

Sodium dithionite is used in the textile industry for the reduction of vat dyes. A considerable excess of sodium dithionite over the stoichiometric amount has to be used (which might be up to 5 times the theoretical amount) as an aqueous solution of sodium dithionite is prone to oxidation in the presence of air.

When sodium dithionite solution containing sodium hydroxide is oxidized with air, the following overall reaction takes place in the liquid phase:

$$O_2 + Na_2S_2O_3 + 2NaOH \rightarrow Na_2SO_3 + Na_2SO_4 + H_2O.$$  (1)

A number of experimental investigations on the kinetics of dithionite oxidation have been reported in literature. Unfortunately, the results reported are in contradiction with each other. This might be due partly to very fast chemical reaction and partly to the differences in the methods of finding the reaction kinetics. While Morello, Cow, Constantine, and Forster (1964) have reported that the reaction is first order with respect to dithionite concentration and zero order with respect to oxygen, Rinker, Gordon, Mason, Sakaida, and Corcoran (1960) have reported that the reaction is half order with respect to dithionite and first order with respect to oxygen. In both cases, the concentration of dithionite was varied from $8 \times 10^{-5}$ to $47.5 \times 10^{-5}$ mol/l and the pH varied from 12.8 to 13.0.

The work of Jhaveri and Sharma (1968) shows the reaction to be first order with respect to dithionite for dithionite concentration below 0.08 M and second order with respect to dithionite for dithionite concentration above 0.08 mol/l. They reported the reaction to be zero order with respect to oxygen concentration for all dithionite concentrations. Recently, Shaikh and Zaidi (1993) reported that the reaction is first order with respect to dithionite when concentration of dithionite was lower than 0.1 M and second order with respect to dithionite concentration when concentration of dithionite was higher than 0.1 M. They too reported the order of reaction with respect to oxygen to be zero for all dithionite concentrations. Camacho, Paez, Blazquez, and Garrido (1992) reported that the order of reaction is zero with respect to oxygen and 1.5 with respect to dithionite. The concentration range of dithionite investigated by these authors is between 0.005 and 0.2 M. Partial pressure of oxygen was higher than 20,260 N/m², pH range was between 12 and 13.7 and temperature varied from 292 to 318 K.
Even though there have been disagreements over the reaction order with respect to dithionite concentration, one can safely conclude from the reviewed literature that the reaction is zero order with respect to oxygen concentration. For the present work, the order of reaction with respect to dithionite concentration was taken to be 1.5 as reported by Camacho et al. (1992) since the operating conditions were similar to those used by these authors.

The kinetic parameter as given by Camacho et al. (1992) is

$$k = 3.22 \times 10^5 \exp\left(-\frac{4250}{T}\right).$$

It has been claimed that a variety of substances such as sodium phosphate, syrupy sodium silicate, pyrogallic acid, ammonium thiocyanate, chloroform, trialkanolamines, manganese compounds, etc. could be used to inhibit the rate of oxidation of dithionite. It is, however, not clear how the presence of these substances inhibits the rate of auto-oxidation of dithionite. In industrial practice, it is clearly desirable to find methods of decreasing the rate of auto-oxidation.

The present investigation, however, deals with oxidation of sodium dithionite with air using a foam-bed contactor, and places emphasis on predicting the performance of the contacting device for a general gas-liquid reaction with zero-order kinetics. It is also perceived that the dithionite oxidation in particular might be useful in studying some fundamental aspects of absorption with chemical reaction, considering that the zero-order kinetics is unique in itself.

The following reactions occur when sodium dithionite is oxidized by atmospheric oxygen:

$$S_2O_4^{2-} + O_2 + 2OH^- \rightarrow SO_3^{2-} + SO_4^{2-} + H_2O.$$  \hspace{1cm} \text{(3)}

$$SO_3^{2-} + \frac{1}{2}O_2 \rightarrow SO_4^{2-}.$$ \hspace{1cm} \text{(4)}

2. Experimental

2.1. Experimental set-up

A typical foam-bed reactor is shown in Fig. 1. In the operation of this contactor, the gas is sparged through a pool of liquid containing a surfactant to generate stable foam. The pool of liquid and the foam above it are designated as the storage and the foam section, respectively. The gas bubbles rise up through the height of foam and break on reaching the foam-gas interface, or the foam-breaker sieve plate coated with isoamyl alcohol. During this time of contact in the foam section, the gaseous reactant species from the limited pockets of gas diffuse into the liquid 8lm and reacts with the solute. The partly reacted liquid disengages from the gas at the top of the foam bed and drains continuously back to the storage section through the network of Plateau borders owing to gravity. The details of the column are given in Table 1.

2.2. Materials used

Octyl phenoxy polyethoxyethanol (Triton X-100) was used as a surfactant. Analar grade sodium dithionite in aqueous solution with excess sodium hydroxide was used as the reactant solute. In the experiment, isoamyl alcohol was used as a foam-breaking agent. Iodine, potassium iodide, sodium thiosulfate, potassium dichromate, formaldehyde, and sodium dichromate were used in chemical analysis of the sample.

2.3. Experimental procedure

At the start of an experimental run, saturated air at 30°C was passed through the column and the system was allowed to reach a steady state. Now the solution of sodium dithionite (500 ml) at the desired concentration was poured into the column through the inlet just above the distributor plate. A known quantity of surfactant was present in this solution. The solution foamed immediately.

To maintain the height of foam at a desired level, a sieve-plate was suspended from the top of the column at the required height. On the sieve plate, a foam-breaking agent was employed in the form of a thin sponge disc soaked in isoamyl alcohol. As the foam attained this height, it collapsed and the released gas escaped through the holes in the plate, whereas the liquid drained down to the storage section through the Plateau borders. The progress of the reaction was determined by withdrawing samples of the reaction mixture in the storage pool at suitable time intervals. At the end of the experimental run, the entire quantity of the reaction mixture was withdrawn.

The samples were analyzed for dithionite concentration iodimetrically. The alkaline solution was 8rst 8xed with formaldehyde. This was then neutralized with acetic acid, a known amount of standard iodine solution was added to this solution, and the excess iodine solution was back titrated against sodium thiosulfate. The details of the method have been reported by the Committee on Analytical Methods (1957).

Liquid holdup was measured experimentally using an inclined manometer. The superficial velocity of air was varied from 4.24 to 6 cm/s. Under these conditions, stable foam was obtained. The foam-bed reactor was operated in the semi-batch mode. The conversion characteristics of the foam-bed reactor were studied at various initial concentrations of sodium dithionite.

3. Model

Various models of foam-bed reactor have been reported in literature (Biswa & Kumar, 1981; Bhaskarwar & Kumar, 1984; Bhaskarwar, 1987; Bhaskarwar, Desai, & Kumar, 1990). The model reported by Biswas and Kumar (1981) is based on an idealized regular pentagonal
The idealization of the reactor is schematically shown in Fig. 2.

The material balance for component B becomes

\[ \dot{V} B = (Q_1 + Q_2) C_B - Q_1 C_{BO} - Q_2 C_{BI}. \]  

(5)

The pertinent diffusion of component A (oxygen, with the present 1.5th order, irreversible chemical reaction) in the \( \tau \)at liquid film is described by the following partial differential equation:

\[ \frac{\partial C_A}{\partial t} + \frac{\partial (C_A \cdot \tau)}{\partial x} = D_A \frac{\partial^2 C_A}{\partial x^2} - k C_A^\frac{1}{2}. \]  

(6)

If the concentration of component B in the liquid film (CB) does not change appreciably during the course of reaction, the rate can be treated as constant and the reaction can be assumed to follow a pseudo-zero-order kinetics. We thus get the following equation for gas absorption with zero-order
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into a number \((N)\) of short-time intervals and integrated equation (16) over the successive time intervals. During a short-time interval, \(M\) does not change appreciably and can be treated as constant and Eq. (16) can be integrated using the value of \(C_B\) obtained from the previous interval as initial value. With this approach the concentration of dithionite in the storage section is given as a function of time for a semi-batch operation of the foam-bed reactor, as

\[
M(t) = M(0) + \int_{0}^{t} \frac{M(t')}{V(t')V(t)} dt' \tag{17}
\]

Eq. (17) is applicable for short time intervals \((t_i\) to \(t_{i+1}\)) and in general \(M\) has to be modified after every such interval. Because of the dithionite-concentration dependent pseudo-zero-order reaction rate, \(r_0\), in this specific case the value of \(M\) must be obtained by a special procedure which involves subdivision of total contact time also into short intervals, calculation of \(M\)'s over successive time intervals assuming constant but different \(r_0\)'s, and addition of \(M\)'s over all intervals to obtain total \(M\).

The calculation of other parameters is based on the bubble radius \((r_b)\) and the average liquid holdup, as given by Bhaskarwar and Kumar (1984). The bubble radius is estimated using the simplified model of bubble formation. The pertinent expressions for calculation of parameters are

\[
V_b = \frac{0.156}{7.66} \left( \frac{Q_g}{6} \right)^{1.2}, \tag{18a}
\]

\[
r_b = \frac{1}{7.537} \left( \frac{nsr_b}{1 - e} \tan(54.9^\circ) \right), \tag{18b}
\]

\[
a = \frac{nsr_b}{7.66} \left( \frac{1 - e}{\tan(54.9^\circ)} \right), \tag{18c}
\]

\[
V = \frac{V_b}{6(1 - e)}, \tag{18d}
\]

The value of average liquid holdup is measured experimentally with the help of an inclined manometer.

4. Results and discussion

Results of numerical simulation for a general zero-order gas-liquid reaction and specific experiments on oxidation of dithionite are discussed in the following two sub-sections.

4.1. Simulation of gas absorption inside foam \(3\)lm

The theoretical predictions were obtained by simulation using Eqs. (14), (15) and (17) in MATLAB. In each simulation, the contact time between liquid \(8\)lm and gas was divided into small periods and the concentration of liquid-phase reactant and hence the rate of reaction was taken constant during each time period. \(M\) was calculated for all such intervals and the concentration of liquid-phase reactant in foam was adjusted for each successive interval using Eq. (15). The total amount of gas dissolved \((M)\) for the total time of contact was obtained by adding up all the values of \(M\) calculated for each short-time interval. It must be emphasized that the 'simulation' here is based on analytical solutions, rather than on the conventional complete numerical discretization schemes.

Fig. 3 shows the temporal development of dissolved gas-concentration profiles inside the rising foam \(8\)lm for physical absorption \((R_0 = 0 \text{ mol m}^{-3} \text{ s})\). The assumed set of values of parameters has been tabulated in Table 2. It can be seen that though the interface between the gas and liquid is always saturated with the dissolving gas as per Henry's law, the concentration of the dissolved gas inside the foam
Table 2
Sets of parameters

<table>
<thead>
<tr>
<th>System parameters</th>
<th>$D_A$</th>
<th>$K_g$</th>
<th>$\gamma_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.75 x $10^{-9}$ m$^2$s</td>
<td>0.0151</td>
<td>1</td>
</tr>
<tr>
<td>Operational parameters</td>
<td>$C_{gi}$</td>
<td>$V_B$</td>
<td>$H$</td>
</tr>
<tr>
<td></td>
<td>1.355 x $10^{-2}$ kg mol=m$^3$</td>
<td>2.2633 x 10$^{-3}$ m$^3$</td>
<td>0.45 m</td>
</tr>
<tr>
<td>Equipment parameters</td>
<td>$r_c$</td>
<td>$N_H$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.5 cm</td>
<td>7</td>
<td></td>
</tr>
</tbody>
</table>

8 lm builds up with time till it reaches its saturation value after which the diffusion stops.

Figs. 4 and 5 depict the effect of chemical reaction on the temporal development of the dissolved unreacted gas-concentration profile inside the foam 8 lm. Fig. 4 shows the resulting concentration profiles when rate of reaction is 0.1 mol=m$^3$ s. As expected the dissolved-gas concentration everywhere inside the foam 8 lm is less than that for physical absorption, at equal time of contact, owing to depletion because of chemical reaction. Since the foam 8 lm is surrounded by limited gas pockets, the concentration of dissolved unreacted gas inside the foam 8 lm starts to deplete at large contact times (e.g. $t_c = 1000$ s) until the entire 8 lm is finally free of this solute. As the rate of zero-order reaction is increased to 1 mol=m$^3$ s (Fig. 5), the dissolved free gas is consumed at a faster rate inside the foam 8 lm and hence it is only able to penetrate a smaller distance inside the 8 lm.

In Fig. 6, the concentration profiles inside the foam 8 lm for two different reaction rates ($r_0 = 0.1$ and 1 mol=m$^3$ s) are compared after the 8 lm has been exposed to the gas for equal time. The concentration profile for diffusion without chemical reaction is also shown for comparison. The reaction clearly reduces the concentration of dissolved free gas everywhere inside the 8 lm, and the greater the reaction rate the smaller is the concentration.

Fig. 7 illustrates the effect of variation of gas flow rate on the concentration gradient inside the foam 8 lm. Since bubble volume and 8 lm thickness increase with an increase in the gas flow rate, an increase in concentration gradient with flow rate may be expected.

In Fig. 8, dissolved unreacted gas concentration has been plotted versus time of contact for different points inside the foam 8 lm. The rate of reaction is same for each case at $r_0 = 0.1$ mol=m$^3$ s. The concentration of gas starts building up later at points that are farther away from the gas-liquid interface. After a sufficiently long contact time the concentration at each point within the 8 lm reaches a quasi-steady value. Under these conditions, the rate of solute depletion because of chemical reaction is equal to the rate at which the solute is replenished because of diffusion.

In Fig. 9, the concentration of dissolved free gas has been plotted against time for two different zero-order reaction rates, viz. 0.1 and 0.2 mol=m$^3$ s, at a fixed location inside the foam 8 lm. The concentration reaches a quasi-steady-state value as in the previous figure, but the effect of reaction is to reduce that value. The lower concentration everywhere inside the foam 8 lm implies a higher concentration gradient and a greater mass transfer rate which compensates for the greater solute-depletion rate due to a faster zero-order chemical reaction. When there is no accompanying reaction, the concentration reaches the saturation value and the equilibrium state of no mass transfer is attained, provided the initial amount of the gas in the two pockets sandwiching the foam 8 lm exceeds its saturation capacity. The simulation results thus broadly corroborate these expectations.

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Figure 4: Concentration profiles inside the 8 lm at different contact times for $r = 0.1$ mol=m$^3$ s.
4.2. Experimental measurements

To experimentally determine the performance of a foam-bed reactor for a zero-order reaction, we have studied the effects of air flow rate and initial dithionite concentration on oxidation of aqueous sodium dithionite solutions. This reaction must satisfy the following inequality to be considered a pseudo-zero order reaction (Hikita & Asai, 1964):

$$\sqrt{M} \ll E_i$$

where

$$M = \left( \frac{2}{m+1} k_m A^* \left( \frac{1}{2} (B^*)^r \right)^{m-1} \right)$$

Substituting the parameters' values, pertinent to the present system, it is found that $\%M$ is at least an order of magnitude smaller than $E_i$. This is a conservative estimate of the desired inequality, as we overestimated the 8lm thickness (of 8lm theory) by equating it to the half foam-8lm thickness. As the later estimate is likely to be an overestimation of the real magnitude by probably an order of magnitude, we may actually have $\%M$ smaller than $E_i$ by about two orders of magnitude. Thus, the pseudo zero-order assumption is justified over short time intervals.
In order for a reaction to lie in fast-reaction regime, the following condition has to be fulfilled (Astarita, 1965):

$$\frac{2}{(f^>)} \frac{D_{aD}}{D} \leq 1,$$  \hspace{1cm} (22)

where $f^>$ is the volume of liquid per unit interfacial area, $D$ the diffusion time $= D_{aD}/k_2$.

Substituting the parameters' values pertinent to the present system, left-hand side is found to be of the order $1 \times 10^{-3}$. Thus the given reaction lies in fast reaction regime.

4.3. Effect of air flow rate on conversion

Fig. 10 shows the effect of superficial air velocity on the conversion of sodium dithionite in the foam-bed reactor obtained experimentally. The initial concentration of sodium dithionite was $83.3 \text{ mol/m}^3$ and superficial air velocity was varied from 4.24 to 5.94 m/s. The liquid holdup was measured to be 0.054 and 0.075, respectively, for the two cases. The height of the bed was maintained constant at 45 cm. Solid lines represent model's prediction (without taking into account conversion in storage section) while the dotted and dashed lines show the model's prediction by taking into account experimentally measured conversions inside storage section when air flow rate is 5 and 7 l/min, respectively. It is seen that the concentration of dithionite in the storage section attained in a given time is lower for a higher superficial air velocity if the foam height and the initial dithionite concentration are held constant. It can be explained by
considering the development of concentration profiles of unreacted oxygen inside the foam 8lm, as it rises through the column. Theoretically, we predict (Fig. 7) the concentration gradient to be higher and depth of penetration to be lower at any time of contact for higher gas flow rate. This effect is primarily due to increase in the thickness of foam 8lm with the increase in gas flow rate (Bhaskarwar & Kumar, 1984). Thus the average concentration gradient of unreacted oxygen inside the foam 8lm over the entire time of contact is higher when the gas flow rate is higher. This results in a greater flux of oxygen to the 8lm, which in turn implies higher conversion of dithionite under diffusion limiting conditions.

4.4. Effect of initial dithionite concentration

The effect of initial dithionite concentration on the conversion of sodium dithionite in the foam-bed reactor has been shown in Fig. 11. The height of foam and the superficial air velocity are held constant here. The initial concentration of dithionite has been varied from 52.08 through 83.33 to 104 mol/m$^3$. Liquid holdup values for the three cases were found to be 0.051, 0.054, and 0.062, respectively. It can be seen that the rate of consumption increases with the increase in initial dithionite concentration. Since the model presented here is for a zero-order reaction, the observation may not be directly evident. But since, as explained
earlier, the dithionite oxidation reaction is of order 1.5 with respect to dithionite concentration, the rate of reaction would be higher for higher dithionite concentrations. This explains the higher rate of consumption for a higher initial dithionite concentration. The theoretical predictions (solid lines) have been obtained, as explained earlier, by using Eq. (17) for small time intervals over which the dithionite concentration (and hence the rate of reaction) is assumed constant and which is modified after every such interval. The dashed lines represent the theoretical predictions accounting also for experimentally measured conversions in storage section in absence of foam. Both the sets of predictions agree with the experimental conversions fairly well.

4.5. Effect of randomly chosen variables on conversion

Figs. 12 and 13 show the effect of simultaneous variation in two parameters (initial dithionite concentration and the superficial air velocity), mainly to assess the model’s predictive capability in the spirit of quality control, on conversion. Bed height was maintained at 45 cm. The theoretical predictions (both without and with experimentally measured conversions in storage section in absence of foam) have been compared with experimental data and are found to be in a reasonably good agreement with the data. The model may therefore be adjudged fairly dependable.
Fig. 13. Effect of variation of two parameters on reactor performance.

**Notation**

- $a$: half-8lm thickness, m
- $A^*$: interfacial concentration of species A, the gas being absorbed, kg mol=m$^3$
- $B^0$: initial concentration of liquid-phase reactant, kg mol=m$^3$
- $C_A$: concentration of dissolved free A (a reactive component) in the 8lm, kg mol=m$^3$
- $C_{A0}$: concentration of reactant A in the gas bubble, kg mol=m$^3$
- $C_B$: concentration of liquid-phase reactant B, kg mol=m$^3$
- $C_{B0}$: inlet concentration of liquid-phase reactant B, kg mol=m$^3$
- $C_{B1}$: concentration of liquid-phase reactant B in the liquid draining into the storage section from the foam section, kg mol=m$^3$
- $D_A$: diffusivity of A in the liquid, m$^2$s
- $E$: parameter defined by Eq. (21), dimensionless
- $f(t)$: unit step function
- $k$: kinetic constant, mol$^{-A}$/m$^{1.5}$/s
- $h$: liquid-phase absorption coefficient, m/s
- $k^*$: reaction rate constant, (m$^3$=kg mol)$^{-1}$/m$^3$, equilibrium distribution factor of A between liquid and gas, dimensionless
- $K_{ds}$: defined in text, m$^{2}$
- $L$: defined in text, equals the representative length of a gas pocket, m
- $M$: amount of gas-phase component A absorbed by the half 8lm, kg mol; parameter defined by Eq. (20), dimensionless
- $P1$: number of holes in distributor plate
- $P2$: defined in text
- $P_{rs}$: non-zero roots of Eq. (13), s$^A$
- $Q$: flow rate of liquid entering the foam-bed reactor, m$^3$s
- $Q1$: flow rate of liquid draining into storage section from the foam section, m$^3$s
- $r0$: zero-order reaction rate, kg mol m$^{-3}$/s
- $-RA$: rate of reaction of A, kg mol m$^{-3}$/s
- $S$: area of a foam 8lm, m$^2$
- $t_c$: time of contact between the 8lm and gas pocket, s
- $t_d$: diffusion time, s
- $V$: volume of liquid in storage section, m$^3$
- $VI$: volume of liquid 8lm in foam section, m$^3$
- $VB$: volume of dodecahedral foam bubble (twelve times the volume of a gas packet), m$^3$
- $x$: one-dimensional spatial coordinate for a system with origin placed at center of the 8lm, m
- $YA$: stoichiometric factor, i.e. moles of liquid-phase reactant B consumed per mole of gaseous-phase reactant A, dimensionless
- $(f>$: volume of liquid per unit interfacial area, m

**Superscripts**

- $'$: equilibrium
- $*$: total, saturation

**Subscripts**

- $g$: gas
- $i, 0$: initial
References


Further reading
