Modelling of a fixed-film tubular photobioreactor for conversion of hydrogen sulphide to elemental sulphur

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Relationships were developed to establish the theoretical basis for scale-up of a fixed-film continuous-flow tubular photobioreactor for removal of hydrogen sulphide from synthetic industrial wastewater and its conversion to elemental sulphur. These are based on experiments with a bench scale reactor where the active part of the reactor was sixteen 150 mm length Tygon tubes. Three different tube sizes (internal diameters of 6.4, 3.2 and 1.6 mm) were used to investigate the effect of tube size on reactor performance. In addition, the washout velocity (the velocity at which fixed-film biomass started to washout) for the 1.6 mm diameter tube reactor was determined. Three models were developed to predict reactor performance and establish the basis for scale-up of the process. All three models predicted reactor performance with a reasonable degree of accuracy.

Keywords: Chlorobium limicola, Fixed-film, Photobioreactor, Phototrophic, Green sulphur bacteria
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Wastewaters from petroleum refineries and pulp mills contain hydrogen sulphide, which must be treated prior to discharge to surface water due to its toxicity to aquatic life and high oxygen demand. Petroleum refineries typically recover elemental sulphur from sour (sulphide-containing) water by the Holmes-Stretford process¹ or by steam stripping followed by the Claus process². These methods are costly and energy intensive due to the requirement of chemical additives and/or the needs of various physical treatment methods such as aeration, heating and centrifuging³.

Biological oxidation of hydrogen sulphide has the potential to overcome these disadvantages. The significant advantages of biological methods over conventional methods are: potentially low operation costs, the absence of toxic chemicals as additives/catalysts and high pressure, high temperature tolerant materials are not required. Syed⁴ summarized the relevant previous studies using both chemotrophic and phototrophic bacteria.

Henshaw et al.⁵ operated a once-through, continuous-flow stirred-tank photosynthetic bioreactor where the liquid influent contained dissolved sulphide. More than 90% of the sulphide was converted to elemental sulphur at loading rates up to 4.4 mg/L.h. They concluded that when comparing results obtained by using reactors of different sizes, the radiant flux (light) per volume is an important parameter in the consumption of sulphide. Further, since the total concentration of bacteria in the reactor plays a key role in sulphide utilization, the parameter: light per volume times bacteria concentration would better represent the capacity of the reactor to consume sulphide.

Using a fixed film, continuous-flow tubular photobioreactor employing Chlorobium limicola and an infrared light source, Henshaw and Zhu⁶ succeeded in removing sulphide from synthetic wastewater at sulphide loadings of 111 to 286 mg/L.h, while 92 to 95% of the influent sulphide was converted to elemental sulphur. Due to the use of an attached growth process, higher green sulphur bacteria (GSB) concentrations were attained which resulted in higher sulphide loadings than when using the suspended growth approach. This process also eliminated the need for separating GSB from the reactor effluent because, for the most part, the biomass remained in the reactor in attached form. For subsequent sulphur recovery, only separation of elemental sulphur from the effluent is required.

Encouraged by the success of this fixed-film tubular photobioreactor, the effect of tube size on its performance was investigated by Syed and Henshaw⁷. Three different tube sizes with internal diameters (ID) of 6.4, 3.2 and 1.6 mm were used to investigate the effect of tube size on reactor performance. The reactor with 1.6 mm tubes attained a higher sulphide loading
rate (1451 mg/L·h) and shorter hydraulic detention time (approximately 7 min) than those previously reported in the literature. This paper focuses on development of models for this photobioreactor system to provide the basis for scale-up of the process, and testing of these models with additional data.

**Experimental Procedure**

**Materials and Methods**

The active part of the fixed-film, continuous-flow photobioreactor consisted of sixteen parallel 150 mm long pieces of Tygon tubing such that all tubes were vertical. In all the experiments, flow through the reactor tubes was upwards. Details of the reactor design and analytical methods have been described previously.

The reactor was operated so that all sulphide in the reactor influent was consumed, yet there was essentially no oxidation of the elemental sulphur produced in the reactor to sulphate. This was termed the optimal sulphide loading rate. This condition was achieved as described by Syed and Henshaw by creating a feed solution of known sulphide and sulphate concentration, and daily adjusting the flowrate until the sulphide concentration in the reactor effluent was zero, but there was no increase in sulphate concentration throughout the reactor. Thus in this study, the independent variables were: light intensity, diameter of reactor tubes, length of the tubes and influent sulphide concentration. The dependent variables were attached bacteriochlorophyll (bchl) concentration, hydraulic detention time and the optimal sulphide loading rate. Sulphide loading rate (SLR) equals the influent sulphide concentration divided by the detention time.

In addition, the reactor with 1.6 mm diameter tubes was used in upflow mode to determine the velocity at which biomass adhering to the tube started to washout. Initially the suspended bchl concentration in the effluent was measured. Velocity was then increased and after observing a significant increase in concentration of suspended bchl in the effluent, velocity was decreased in two steps to the normal operating range. Velocity was then increased to the previous maximum level to reconfirm the washout of the biomass at that velocity.

**Results**

Table 1 shows the values of the relevant independent and dependent variables at steady state condition – after the optimal condition had been maintained for 48 successive hours. It shows that increased optimal sulphide loading rate (OSLR) was observed with an increase in light intensity. For the 1.6 mm diameter tube reactor, a 29.5% increase in optimal sulphide loading rate was observed when light intensity was changed from 80.3 to 116 W/m² (44.4% increase). Comparing Runs 8, 9 and 10 to Run 12, the decrease in OSLR was 27% while light intensity changed 24% (152 to 116 W/m²). For the 3.2 mm diameter tube reactor, a 42.4% decrease in optimal sulphide loading rate (average of Runs 5 and 6) was observed when light intensity was changed from 152 to 76.4 W/m² (49.7% decrease). Figure 1

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Light intensity (W/m²)</th>
<th>Light per volume (W/L)</th>
<th>Diameter (mm)</th>
<th>Attached bchl (mg/L)</th>
<th>Influent sulphide conc. (mg/L)</th>
<th>Detention time (min)</th>
<th>OSLR (mg/L·h)</th>
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<tr>
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Note: bchl = fixed film bacteriochlorophyll (attached bchl mass divided by reactor tube volume), OSLR = optimal sulphide loading rate, Run 4 was terminated due to clogging of the tubes.
shows the relationship between light intensity and optimal sulphide loading rate for different diameter tube reactors.

Optimal sulphide loading rate increased with decreased tube diameter as shown in Fig. 2. With the variation of diameter, two important parameters, light per volume and attached bchl concentration varied. At a constant light intensity, light per volume will increase in proportion to the decrease in diameter of the tubes. This inverse proportional relationship follows the projected-area/volume ratio as the tube size changes.

Attached bchl concentration increased with a decrease in tube diameter as shown in Fig. 3. Based simply on geometry, the surface area/volume ratio of a tube is also inversely proportional to the tube diameter. Attached bchl concentration increased about 2.4 times (considering the runs at light intensity 152 W/m²) when the tube size in the reactor was changed from 6.4 to 3.2 mm whereas the concentration increased 1.2 times when the tube size in the reactor was changed from 3.2 to 1.6 mm. For this calculation, the average attached bchl concentrations (of Runs 1, 2 and 3 for the 6.4 mm diameter tube, of Runs 5 and 6 for the 3.2 mm diameter tube and of Runs 8, 9 and 10 for 1.6 mm diameter tube) were used. These values can be put into perspective by calculating the values of attached bchl mass per wetted area (mg bchl/mm²) which were on average 2760, 3310 and 1990 for tube diameters 6.4, 3.2 and 1.6 mm, respectively. These numbers were calculated by multiplying the attached bchl concentration (extracted mass of bchl divided by tube sample volume) by the volume of the tube and dividing by the wetted area inside the tube and are an indication of the thickness (or density) of the biofilm. The highest thickness occurs in the 3.2 mm diameter tube. The bacteriochlorophyll density seems to be increasing with decreasing tube size (6.4 to 3.2 mm) but the density in the 1.6 mm tube may be limited by shearing due to the higher fluid velocities (>20 mm/min) encountered in the 1.6 mm diameter tube as compared to the 3.2 and 6.4 mm diameter tubes.
Attached bchl concentration is very important regarding consumption of sulphide since it is a measure of concentration of GSB. Fig. 3 also shows the relationship between attached bchl concentration and optimal sulphide loading rate for different diameter tube reactors involving Runs (1, 2, 3, 5, 6, 8, 9 and 10) at a constant light intensity (152 W/m²). Since both of these variables have the volume of the tubes, in L, in their denominators, comparing them can result in conclusions that are independent of volume. Thus, the slope of this curve in Fig. 3 represents the change in throughput of sulphide (in mg/h) for each unit increase in mass (mg) of bchl. As a parameter to predict attached bchl concentration, OSLR is probably superior to tube diameter, due to the higher correlation and more consistent trend.

It is interesting to note that at the same light intensity (152 W/m²), the optimal sulphide loading rate in the 3.2 mm tube diameter reactor increased about 5 times (considering the average of the runs concerned) over that in the 6.4 mm diameter tube reactor although attached bchl concentration increased only about 2.4 times. The optimal sulphide loading rate in the 1.6 mm tube diameter reactor increased about 2.4 times (considering the average of the runs concerned) compared to that in the 3.2 mm diameter tube reactor although attached bacterial concentration increased only about 1.2 times. The rate of increase of optimal sulphide loading rates due to the reduction in tube diameter is much higher than the rate of increase of attached bchl concentrations. Assuming that bacteria control the reaction rate, it seems that an increase in bchl concentration alone is not solely responsible for the increased OSLR in smaller tubes. For example, the OSLR/bchl ratio in the 1.6 mm diameter tube is 0.86 whereas in 3.2 and 6.4 mm diameter tubes, the ratios are 0.5 and 0.22, respectively. This increase in OSLR due to reduction of tube diameter at an equivalent attached bchl concentration has been explained by Syed and Henshaw. Accordingly, in smaller diameter tubes, shorter time was required for diffusion of sulphide from the bulk liquid to the liquid-biofilm interface for consumption by the bacteria. However, the greater scattering of light in larger tubes may also be a factor. An experiment was performed to determine the velocity at which biomass adhering to the tubes started to washout. This critical velocity indicates the maximum operating flowrate for the reactor. The experimental results are shown in Fig. 4. At a velocity (in a single tube) of 44 mm/min, bacteria detachment occurred as can be observed from the two peaks in suspended bchl concentration in this figure. Unlike the effluent of other runs, where suspended bchl concentration varied between 0.2 to 0.46 mg/L, effluent at these flowrates was visibly green. So, this velocity was above the critical or washout velocity for the 1.6 mm diameter tubes. Operating velocity during reactor operation should always be lower than this velocity. In fact, 38 mm/min might be considered the maximum operating velocity because at this tube velocity, effluent suspended bchl value was still low. This washout velocity limits the length of the tubes for a given detention time since the detention time can be equated to the tube length over the velocity. So, there is a limit regarding the velocity of flow and the length of the tubes. This issue must be taken into account while scaling up the process. The velocity parameter was not included in model formulation since it can be represented by the parameters detention time, diameter and length.

There was no relationship between the optimal sulphide loading rate and the influent sulphide concentration within the range used. The linear correlation coefficient \((R^2)\) between these two parameters is only 0.18, which indicates no correlation. Other parameters, such as light intensity play a larger role in determining OSLR than sulphide concentration. Therefore, this parameter was also not used explicitly in model formulation. Moreover, optimal sulphide loading rate indirectly incorporates influent sulphide concentration and detention time in the models.
Model development

Three models using three different approaches have been developed to provide a design tool for the photobioreactor system.

Linear model

Model formulation

A simple linear regression between optimal sulphide loading rate and the product of light per volume \(L_v\) and attached bacteriochlorophyll concentration (bchl) using data from Runs 1 to 12 (Table 1) resulted in Eq. (1). The line of best fit was forced through zero because with zero bacteria, there would be no consumption of sulphide and therefore the OSLR would be zero.

\[
\text{OSLR (in mg/L.h)} = 7.29 \times 10^{-3} \times \text{bchl} \times L_v \quad \text{(1)}
\]

where bchl is in mg/L. Now,

\[
L_v = \frac{LI \times d \times Le \times n}{n \times \pi / 4 \times d^2 \times Le \times 1000} = 1.273LI / d \quad \text{(2)}
\]

where \(LI\) = light intensity (W/m\(^2\)), \(d\) = tube diameter (mm), \(Le\) = length of tubes and \(n\) = number of tubes. Substituting Eq. (2) into Eq. (1) results in,

\[
\text{OSLR} = 9.28 \times 10^{-3} \times LI \times d^{-1} \times \text{bchl} \quad \text{(3)}
\]

Eq. (3) is the linear model, which predicts the steady-state sulphide loadings for different diameter tube sizes and at different light intensities when effluent sulphide concentration is zero and when there is no significant difference between influent and effluent sulphate concentrations.

Model evaluation

The model was first evaluated using the data from Runs 1 to 12. Predicted results for different tube size reactors are shown in Fig. 5. Following the equation \(\text{ESS} = \Sigma \text{observed values–calculated values}\)^2, the error sum of squares (ESS) was calculated\(^9\). The ESS value for linear model was 26,582. The percentage error [(difference between observed value and calculated value \(\times 100)/\text{observed value}] varied between 0.4 to 17.5%.

Polynomial model

Model formulation

A second order polynomial regression was applied to data from Runs 1 to 12, resulting in the following equation:

\[
\text{OSLR} = -0.83 \times 10^{-8} [(LI/d) \times \text{bchl}]^2 \\
+ (103.7 \times 10^{-4})(LI/d) \times \text{bchl} \quad \text{(4)}
\]

Units of the parameters mentioned in the polynomial model are the same as in the linear model, and again, the line was forced to pass through the origin.

Model evaluation

The model was evaluated using the data from Runs 1 to 12. Predicted results for different tube size reactors are shown in Fig. 5. The ESS for the polynomial model was 18,740, which is lower than for the linear model. The error varied between 0.75 to 24%.

Non-dimensional model

Dimensionless parameters

A third model was developed by grouping variables into dimensionless parameters and finding an empirical relationship between the dimensionless parameters. The dimensionless parameter components were then substituted back into the empirical equation to develop a relationship between the original variables. The procedure used the method of Szirtes\(^9\). The relevant variables (seven) were: diameter \((d\) in m\) of the tubes, attached bacteriochlorophyll concentration (bchl in mg/L), light per volume \((W/L)\), diffusion coefficient \((D\) in m\(^2\)/min\), length of the tubes \(Le\) in m), optimal sulphide loading rate \((\text{SLR in mg/L.min})\) and yield coefficient \((Y\) in mg bchl/mg S\(^2\).W). For the
purpose of this analysis, yield coefficient, an independent and uncontrolled parameter, is defined as the ratio of the mass of cells formed to the mass of substrate consumed times radiant flux, since the growth of phototrophic bacteria depends not only on the amount of substrate but also on the intensity of light.

The variables were written in a row from left to right starting with the dependent variable (OSLR in this case) as shown in Fig. 6. The relevant dimensions were written in a column on the left. The dimensional matrices (A and B) were filled in. Each matrix element is the exponent of a particular variable’s dimension. The “A” matrix, which is the rightmost determinant of order 5 (number of the dimensions), describes the independent parameters. The “B” matrix, which is formed by the remaining elements, defines the independent parameters. The “C” matrix was calculated following the fundamental formula, C = [A−1·B]T, where A−1 is the inverse of A, the superscript T designates the transpose of the matrix and the symbol · indicates matrix multiplication.

Figure 6 shows the matrices A, B, C and the identity matrix D. In this case, the number of independent dimensionless variables is two (number of variables–number of dimensions). Two dimensionless variables using the elements of the C and D matrices were formed which are:

\[ q_1 = \frac{\text{OSLR} \cdot Y}{\text{bchl} \cdot (W/L) \cdot D \cdot e} \]  \hspace{1cm} \text{(5)}

and

\[ q_2 = \frac{d}{Le} \]  \hspace{1cm} \text{(6)}

where \( q_1 \) is designated as the capacity number and \( q_2 \) is designated as diameter-length ratio or the inverse of the aspect ratio of the tubes.

Model formulation
Since the values of \( Y \) and \( D \) are unknown, \( Y/Dq_1 \) versus \( q_2 \) was plotted in a graph using the experimental results from 1 to 12 (Table 1). The relationship \( Y/Dq_1 = 19195.\exp(2.68q_2) \) was obtained by using the exponential fit function in an Excel spreadsheet. Substituting the values of \( q_1 \) and \( q_2 \) into this relationship, Eq. (7) is obtained, which is the non-dimensional model.

\[ \text{OSLR (mg/L·h)} = \frac{(\text{bchl}) \cdot (W/L) \cdot Le}{19195 e^{2.68q_2}} \]  \hspace{1cm} \text{(7)}

Model evaluation
The model was evaluated using the data from Runs 1 to 12 (Table 1). Prediction results for different tube size reactors are shown in Fig. 5. The ESS value for the non-dimensional model was 38862 and the error varied between 0 and 13.2%.

Model testing
The models were tested using experimental results of three additional runs (NR-1 to NR-3 in Table 1), which were not used in the formulation of the models. The results are shown in Fig. 7, which shows that the predictions by all the three models are satisfactory.
Discussion

The ESS values calculated during model evaluation were 26582, 18740 and 38862 for the linear, polynomial and non-dimensional models, respectively. In addition, using the three additional data points for testing, the ESS values were 2411, 1691 and 1153 for the linear, polynomial and non-dimensional models, respectively. So, there is no significant difference in performance of the three models. Moreover, an $F$-test\textsuperscript{10,11} was performed to decide whether the use of the additional parameter (square of $L/bchld/bchcl$) in the polynomial model compared to the linear model was justified or not. The test revealed that the greater accuracy achieved by adding the additional parameter is not significant at the 95\% level. As mentioned before, optimal sulphide loading rate is determined by influent sulphide concentration and detention time. For a particular wastewater flowrate, knowing the detention time, the reactor volume can be calculated. The maximum tube length can then be determined using the maximum operating velocity. The diameter and number of the tubes can be chosen afterwards based on the volume required. For a particular tube diameter, attached bacteriochlorophyll concentration is expected to be in the range of the experimental results of this study although Fig. 3 may be used to predict the attached bchl concentration at the design OSLR. So, for a particular or varying optimal sulphide loading rate, after knowing or selecting other parameters, one can adjust the light intensity required.

Conclusions

From the results of present study it can be concluded that the proposed models provide a useful insight about the interrelation of the parameters responsible for sulphide consumption in the photobioreactor. Linear and polynomial models establish the relationship between light intensity, attached bacteriochlorophyll concentration, tube diameter and optimal sulphide loading rate. The non-dimensional model also shows a unique relationship between attached bacteriochlorophyll concentrations, light per volume, tube length, diameter and sulphide loading rate. If the values of diffusion and yield coefficients are measured, a more complete model including these parameters can be developed following the method mentioned before. Unfortunately, none of the models explicitly address the fact that there exists a critical velocity, which cannot be exceeded during the reactor operation to prevent biomass washout.

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References