Dynamic simulation of benzene vapor treatment by a two-phase partitioning bioscrubber
Part I: Model development, parameter estimation, and parametric sensitivity

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Abstract

A dynamic, mechanistic model has been developed to predict the performance of a liquid–liquid, two-phase partitioning bioscrubber (TPPB) for removal, and subsequent biodegradation, of toxic volatile organic compounds (VOCs) from industrial waste gases under various conditions of practical relevance. TPPBs, which contain an immiscible and biocompatible organic liquid phase, allow enhanced biodegradation rates to be maintained by partitioning inhibitory substrates away from microorganisms. The system being considered involves the treatment of benzene vapors by *Achromobacter xylosoxidans* Y234 using *n*-hexadecane as the organic phase. The model incorporates the following dynamic elements: volatile substrate and oxygen absorption by both liquid phases, partitioning of dissolved substrate and oxygen between liquid phases, and microbial consumption of dissolved substrate and oxygen in the aqueous phase for both growth and maintenance. Part I focuses on the development of the model equations and estimation of relevant parameters. Using parametric sensitivity analysis, the relative influences of the parameters are identified under transient and steady state conditions. Both the organic phase volume fraction and its properties are predicted to have a significant influence on performance. Biocatalysts capable of maintaining high biodegradation rates under dilute substrate concentrations are predicted to be superior for use in TPPBs.
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1. Introduction

Removal and treatment of volatile organic compounds (VOCs) from industrial waste gases is of the utmost importance, given the environmental and human health risks associated with exposure to these hazardous compounds. In response to increasingly stringent government regulations [1], numerous biotechnologies have emerged for reducing industrial VOC emissions. Biologically based alternatives offer advantages over physicochemical counterparts such as low capital and operating costs, innocuous by-products, and greater public acceptance as environmentally friendly processes [2].

The two-phase partitioning bioscrubber (TPPB) is an emerging biotechnology developed to treat waste gases that has shown promise for removing toxic VOCs, such as benzene. The high performance potential of TPPBs is due to enhanced rates of absorption of hydrophobic VOCs [3] and dissolved oxygen [4], as well as biodegradation by their ability to maintain sub-inhibitory conditions when treating toxic compounds [5]. The TPPB and its primary physical and biological constituents are illustrated in Fig. 1. Two-phase partitioning bioscrubbers are characterized by a cell-containing aqueous phase, as well as an immiscible, biocompatible, non-bioavailable organic phase that serves as a reservoir to buffer the cells against high concentrations of toxic substrates. Other key features of an effective organic second phase, as well as a useful protocol for its selection, have been previously described [6]. VOC substrates are captured in the TPPB through absorption as the waste gas passes through the liquid phases, preferentially accumulating in the organic phase. Substrate then partitions into the aqueous phase at greatly reduced concentrations, being delivered at rates which are dictated by the metabolism of the cells [7,8].

Previous studies have demonstrated that TPPBs can effectively treat waste gases containing high concentrations of

Nomenclature

C_A	dissolved oxygen concentration in the aqueous phase (mg O_2 L^{-1})
C_A^*	aqueous dissolved oxygen concentration equilibrated with gas phase (mg O_2 L^{-1})
C_G^{in}	influent gas oxygen concentration (mg O_2 L^{-1})
C_G^{out}	effluent gas oxygen concentration (mg O_2 L^{-1})
C_O	dissolved oxygen concentration in the organic phase (mg O_2 L^{-1})
C_O^*	organic dissolved oxygen concentration equilibrated with gas phase (mg O_2 L^{-1})
D_C	dissolved oxygen aqueous-organic partitioning coefficient
D_S	dissolved substrate aqueous-organic partitioning coefficient
H_{CA}	Henry's Law coefficient of oxygen in the aqueous phase
H_{Ci}	Henry's Law coefficient of oxygen in the phase i
H_{CO}	Henry's Law coefficient of oxygen in the organic phase
H_{SA}	Henry's Law coefficient of substrate in the aqueous phase
H_{Si}	Henry's Law coefficient of substrate in the phase i
H_{SO}	Henry's Law coefficient of substrate in the organic phase
k_d	instantaneous specific rate of endogenous metabolism (h^{-1})
$k_L a_{CA}$	lumped, volumetric mass transfer coefficient of oxygen absorption in the aqueous phase (h^{-1})
$k_L a_{Ci}$	lumped, volumetric mass transfer coefficient of oxygen absorption in the phase i (h^{-1})
$k_L a_{CO}$	lumped, volumetric mass transfer coefficient of oxygen absorption in the organic phase (h^{-1})
$k_L a_{SA}$	lumped, volumetric mass transfer coefficient of substrate absorption in the aqueous phase (h^{-1})
$k_L a_{Si}$	lumped, volumetric mass transfer coefficient of substrate absorption in the phase i (h^{-1})
$k_L a_{SO}$	lumped, volumetric mass transfer coefficient of substrate absorption in the organic phase (h^{-1})
K_C	half-saturation constant of oxygen (mg O_2 L^{-1})
K_I	inhibition constant of the Andrews kinetic model (mg substrate L^{-1})
K_S	half-saturation constant of substrate (mg substrate L^{-1})
m_C	specific maintenance rate on oxygen (mg O_2 mg cells^{-1} h^{-1})
m_S	instantaneous specific exogenous maintenance rate on substrate (mg substrate mg cells^{-1} h^{-1})
M_S	total specific rate maintenance on substrate (mg substrate mg cells^{-1} h^{-1})
n	empirical parameter of the Luong kinetic model
N	bioreactor agitation rate (rpm)
p_j	model parameter j
Q_G	aeration rate (L/h)
s_{ij}	sensitivity coefficient variable i with respect to parameter j
S_A	dissolved substrate concentration in the aqueous phase (mg substrate L^{-1})
S_A^*	aqueous dissolved substrate concentration equilibrated with gas phase (mg substrate L^{-1})
S_G^{in}	influent gas substrate concentration (mg substrate L^{-1})
S_G^{out}	effluent gas substrate concentration (mg substrate L^{-1})
S_m	inhibitory substrate concentration of the Luong kinetic model (mg substrate L^{-1})
S_O	dissolved substrate concentration in the organic phase (mg substrate L^{-1})
S_O^*	organic dissolved substrate concentration equilibrated with gas phase (mg substrate L^{-1})
t	time (h)
V_A	aqueous volume of the single-phase bioreactor (L)
V_G	entrained gas hold-up volume (L)
V_H	headspace volume of the single-phase bioreactor (L)
V_T	total liquid volume of the TPPB (L)
x_i	model state variable i
X	biomass concentration (mg cells L^{-1})
y_i	model output variable i
$Y_{X/C}$	biomass-to-oxygen yield coefficient (mg cells mg O_2^{-1})
$Y_{X/S}$	biomass-to-substrate yield coefficient (mg cells mg substrate^{-1})

Greek letters

ϕ_{ORG}	organic phase volume fraction
μ	specific growth rate (h^{-1})
μ_{max}	maximum specific growth rate (h^{-1})

benzene [9,10], toluene [9], and ethylbenzene [10] as single substrates as well as a benzene–toluene mixture [11] during constant operation. More recently, the dynamic behavior of the TPPB has been investigated using transient benzene feeds [12]. However, since few fundamental investigations have been conducted using the TPPB no definitive conclusions can be drawn regarding which of the many constituent physical and biological phenomena are predominantly responsible for its underlying performance, or under which conditions it can favorably operate. Formulating a conceptual understanding of TPPB operation is most effectively accomplished through the development of a mechanistic mathematical model. Although several partitioning bioreactor and bioscrubber models have been previously developed to describe all or part of their operation [3,13,14], none exist which adequately represent the proposed process configuration or operating conditions.
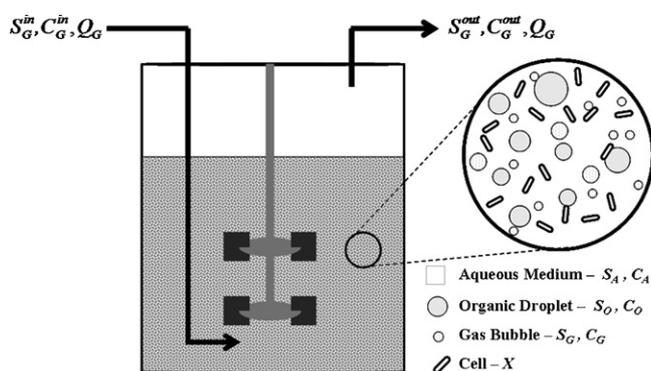
Fig. 1. Illustration of the two-phase partitioning bioscrubber (TPPB).

Part I of this work describes the development of a dynamic model of the TPPB from its fundamental constituent physical and biological phenomena, as well as the procedures used to estimate the relevant parameters. The model will be presented in as generic a form as possible in order retain its broad utility. Since the proposed TPPB model contains many parameters characterizing various physical and biological functions, it becomes difficult to predict a priori how these individual parameters will affect the model predictions. A parametric sensitivity analysis is used to provide valuable insight regarding the relative influence of each of the model parameters during various operating modes. Obtaining a greater fundamental understanding of this process is a major objective of this study, as well as a critical element in the development all vapor-phase bioreactor processes [15]. In Part II of this manuscript, the proposed model is calibrated and validated using experimental data before exploring the predicted performance of the TPPB through a series of simulation exercises.

2. Model development

From the configuration shown in Fig. 1, the TPPB is essentially operated as a liquid–liquid partitioning bioreactor into which the VOC substrate and oxygen are both continuously and solely introduced through absorption from the gas stream while the liquid contents effectively remain as a closed system. Interactions between the relevant physical and biological elements of the model are shown in Fig. 2. Since concentration, composition, and flow rate variations all routinely arise in industrial waste gases, VOC removal processes will be required to operate satisfactorily under transient conditions [16]. Likewise, a useful mechanistic model should produce adequate predictions in response to these fluctuations and, therefore, must be dynamic in nature.

3. Key model assumptions

Several simplifying assumptions, outlined below, are made to develop this model to ensure that it is both sufficiently detailed and mathematically tractable.

(1) Negligible volume change is experienced in the aqueous and organic phases.
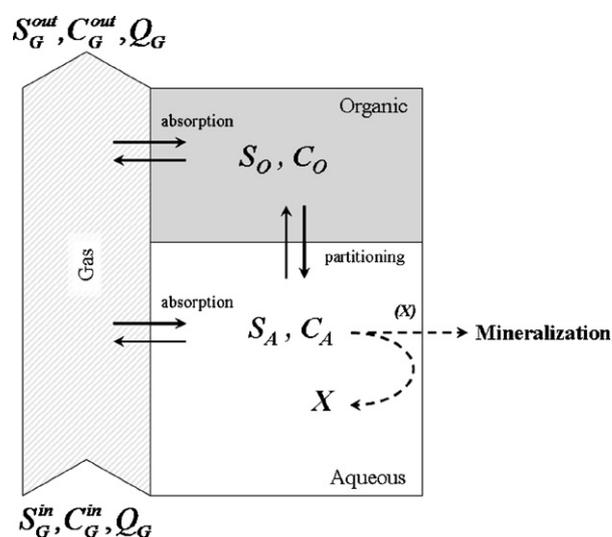

Fig. 2. Schematic representation of key phenomena represented in the proposed two-phase partitioning bioscrubber model. Solid and dashed lines indicate physical and biological processes, respectively.

(2) The organic phase is immiscible and biocompatible, but not bioavailable so that cell growth is neither hindered nor supported by its presence.

(3) All phases are well-mixed. Gas and organic phases are fully dispersed throughout the continuous aqueous phase.

(4) Rates of substrate and dissolved oxygen partitioning between liquid phases are sufficiently high that spontaneous liquid–liquid phase equilibrium can be assumed under all conditions. Validation of this assumption was previously provided for VOCs in a similar two-phase system by Cesario et al. [3].

(5) Dilute solutions allow liquid–liquid and gas–liquid partitioning equilibria driving forces to maintain constant proportionalities, for example, via Henry's Law-type relationships.

(6) Substrate and oxygen absorption rates are controlled by the liquid contribution to the overall mass transfer resistance [17].

(7) Gas hold-up volumes are constant under constant conditions.

(8) Microbial activity is sufficiently described using an unstructured kinetic model.

(9) While specific growth rates are proportional to the aqueous substrate concentration, according to a model to be described later, they are also assumed to depend upon the dissolved oxygen concentrations in an interactive manner using a Monod-type expression in a dual-substrate model [18].

(10) Substrate and dissolved oxygen consumption are distributed between both the biosynthetic and maintenance energy consuming activities of the cell in a manner originally described by Pirt [19]. Previous studies have confirmed the validity of this approach for benzene [10] and dissolved oxygen [20] consumption in the TPPB.

(11) The total cellular maintenance energy requirement, M_S, remains constant. When an excess of exogenous substrate is available, maintenance energy requirements are satisfied by direct substrate consumption while endogenous metabolism supplements the requirements by consuming internal storage materials under starvation conditions. The following relationships, based on the model of Dias et al. [21], is proposed to predict both exogenous and endogenous metabolic rates, respectively, as a function of the specific growth rate:

$$m_S = M_S \frac{\mu}{\mu_{max}} \tag{1}$$

$$k_d = Y_{X/S} M_S \left(1 - \frac{\mu}{\mu_{max}} \right) \tag{2}$$

This relationship assumes that cellular storage materials contain similar carbon content as the rest of the cell.

(12) All cells have a uniform average composition, are freely suspended, do not form flocs, and behave identically. Apart from endogenous decay of biomass, viability losses are neglected.
(13) Additional required inorganic nutrients are always available in excess.
(14) The only terminal products formed from the aerobic substrate biodegradation are cells, H_2O, and CO_2.
(15) Temperature and pH are constant.

The relevant assumptions pertaining to biphasic oxygen absorption in this TPPB process have been previously validated and discussed for the materials used in this TPPB system [22]. Typically, the individual effects of exogenous substrate consumption for maintenance energy and endogenous decay are indistinguishable because they each produce a reduced biomass-to-substrate yield. However, each of these unique biological phenomena yield differing results, particularly should transient starvation periods be studied [23]. Although the total maintenance energy requirements, M_S, remain constant, the supply of energy for these essential functions is now predicted to be derived from exogenous consumption when substrate supplies are plentiful or endogenous decay of storage materials when the substrate becomes depleted. The use of a specific growth rate-dependent expression to simulate exogenous and endogenous rates of metabolism in support of maintenance functions has also been proposed [24–26].

4. Material balance equations

4.1. Material balance on biomass (X)

The rate of biomass accumulation in the TPPB is described by:

$$(1 - \phi_{ORG})V_T \frac{dX}{dt} = \mu X(1 - \phi_{ORG})V_T - k_d X(1 - \phi_{ORG})V_T \tag{3}$$

The form of the empirical model used to predict the specific growth rate as a function of the benzene concentration will be specified following an investigation of the growth kinetics in batch culture. The aqueous dissolved oxygen concentration, C_A, will also affect the specific growth rate as:

$$\mu(S_A, C_A) = \mu(S_A) \frac{C_A}{K_C + C_A} \tag{4}$$

where $\mu(S_A)$ is the particular functional dependence of S_A alone on μ, to be determined experimentally in the presence of excess dissolved oxygen.

4.2. Material balance on dissolved VOC substrate (S_A, S_O)

According to the assumption of spontaneous equilibrium, the dissolved substrate material balance in the biphasic media can be described with respect to the aqueous phase as:

$$((1 - \phi_{ORG}) + D_S\phi_{ORG})V_T \frac{dS_A}{dt}$$
$$= k_L a_{SA}(S_A^* - S_A)(1 - \phi_{ORG})V_T + k_L a_{SO}(S_O^* - S_O)\phi_{ORG}V_T$$
$$- \frac{1}{Y_{X/S}} \mu X(1 - \phi_{ORG})V_T - m_S X(1 - \phi_{ORG})V_T \tag{5}$$

while the dissolved substrate concentration in the organic phase is instantaneously established in linear proportion to the aqueous concentration:

$$S_O = D_S S_A \tag{6}$$

The liquid–liquid partitioning coefficient, D_S, is defined as

$$D_S = \frac{S_O}{S_A} \tag{7}$$

which at equilibrium can be calculated as the ratio of the Henry's Law coefficients ($D_S = H_{SA}/H_{SO}$). The saturation concentrations of the VOC substrate in the liquid phases, S_A^* and S_O^*, are correlated with the gas stream via equilibrium relationships whose most appropriate form will be determined by preliminary mass transfer experiments which will be discussed.

4.3. Material balance on gaseous VOC substrate (S_G)

The substrate concentration in the well-mixed entrained gas can then be calculated as:

$$V_G \frac{dS_G}{dt} = Q_G S_G^{in} - Q_G S_G^{out} - k_L a_{SA}(S_A^* - S_A)(1 - \phi_{ORG})V_T$$
$$- k_L a_{SO}(S_O^* - S_O)\phi_{ORG}V_T \tag{8}$$

4.4. Material balance on dissolved oxygen (C_A, C_O)

The material balance on dissolved oxygen in the biphasic system is treated in an analogous manner to that of the dissolved substrate. Under the modeling assumptions stated earlier,

the oxygen material balance with respect to the aqueous phase becomes:

$$((1 - \phi_{ORG}) + D_C\phi_{ORG})V_T \frac{dC_A}{dt}$$

$$= k_L a_{CA}(C_A^* - C_A)(1 - \phi_{ORG})V_T$$

$$+ k_L a_{CO}(C_O^* - C_O)\phi_{ORG}V_T - \frac{1}{Y_{X/C}}\mu X(1 - \phi_{ORG})V_T$$

$$- m_C X(1 - \phi_{ORG})V_T \tag{9}$$

where by the spontaneous equilibrium assumption:

$$C_O = D_C C_A \tag{10}$$

The liquid–liquid equilibrium is again defined by the partitioning coefficient of oxygen, D_C, according to:

$$D_C = \frac{C_O}{C_A} \tag{11}$$

which at equilibrium can also be calculated as the ratio of the Henry's Law coefficients ($D_C = H_{CA}/H_{CO}$). C_A^* and C_O^* represent the dissolved oxygen concentrations of each phase that are each in equilibrium with gas concentration (C_G^{in}) which can be predicted according to Henry's Law under dilute conditions as:

$$C_i^* = \frac{C_G^{in}}{H_{Ci}} \tag{12}$$

where H_{Ci} represents the Henry's Law coefficient of phase i (aqueous $i = A$, organic $i = O$). Since waste gases are generally rich in oxygen and because only a small fraction of oxygen from the gas phase is actually removed via absorption into the liquid phase, it is typically assumed that $C_G^{in} \approx C_G^{out}$. This approximation leaves little ambiguity as to the proper choice of concentration for use in the mass transfer driving force of Eq. (12). However, as will be discussed, the same general assumption cannot automatically be made when modeling much more dilute VOCs.

5. Model simplification

As will be experimentally demonstrated, for the regimes under which the TPPB is typically operated, sufficiently long gas residence times and high gas–liquid interfacial areas allow the entrained gas-phase benzene concentration to rapidly change from its inlet to its exit concentration. Under the conditions for which a constant gas hold-up is maintained, the rate of change of benzene within the entrained gas can be neglected in Eq. (8). This quasi-steady-state approximation allows the effluent gas benzene concentration to be calculated by:

$$S_G^{out} = S_G^{in} - k_L a_{SA}(S_A^* - S_A)(1 - \phi_{ORG})\frac{V_T}{Q_G}$$

$$- k_L a_{SO}(S_O^* - S_O)\phi_{ORG}\frac{V_T}{Q_G} \tag{13}$$

This simplification reduces the number of differential equations which require simultaneous solution, and eliminates the parameter V_G. Note that the above simplification may not always

be appropriate, but will be shown to be suitable for the range of conditions thus far investigated experimentally using the TPPB (primarily using relatively low aeration rates). With these changes, the combined TPPB model can now be represented by the material balances of Eqs. (3), (5), (9), and (13), which require simultaneous solution.

6. Initial conditions

Typical TPPB operation begins with inoculation and setting of the desired benzene loading rate. However, since the culture routinely experiences a lag phase which lasts 10–12 h (data not shown), benzene is not initially degraded, but accumulates in the liquid phases as it continues to be absorbed. At the end of the lag phase, however, dissolved benzene is rapidly consumed and benzene removal quickly achieves high efficiencies. Since an unstructured growth model is unable to describe the lag phase, when modeling operation from start-up, the initial conditions will reflect those of the TPPB as it reaches the end of the lag period where dissolved and off-gas benzene concentrations are substantial and the biomass is present at its inoculum concentration. Experimental and modeling investigations of transient TPPB behavior have been exclusively performed beginning from a pseudo-steady-state which corresponds to the characteristic 'maintenance state' of the culture [12] in order to provide a consistent point of reference.

7. Parametric sensitivity analysis

Dynamic sensitivity analyses rely upon calculation of the sensitivity coefficients, s_{ij}, which are defined as the partial derivatives of the state variables (x) with respect to the parameters (p) [27,28]:

$$s_{ij} = \frac{\partial x_i}{\partial p_j} \tag{14}$$

The sensitivity coefficients can vary over time, and describe the change in the state variable that would occur at a particular instant due to an incremental perturbation in the parameter. Sensitivity coefficients of a dynamic model can be estimated by numerous methods, although the 'Direct Method', described by Dickinson and Gelinas [29], was selected because it is considered to be of greater computational rigor. According to the Direct Method, the model differential equations are supplemented with the differential sensitivity equations and the complete set are solved simultaneously to obtain both the model predictions and the sensitivities.

Consider the proposed TPPB model in the following general form:

$$\frac{dx}{dt} = g(x, t, p), \qquad y = h(x, p), \qquad x(t_0) = x_0 \tag{15}$$

where y are the output, or measured variables. The differential sensitivity equations are defined as:

$$\frac{\partial s_{ij}}{\partial t} = \sum_{k=1}^{n} \frac{\partial g_i}{\partial x_k} s_{kj} + \frac{\partial g_i}{\partial p_j} \tag{16}$$

The sensitivities of the output responses can then be calculated as:

$$\frac{\partial y_i}{\partial p_j} = \sum_{k=1}^{n} \frac{\partial h_i}{\partial x_k} s_{kj} + \frac{\partial h_i}{\partial p_j} \qquad (17)$$

Sensitivity coefficients are often normalized as $(p_j/y_i)(\partial y_i/\partial p_j)$ to remove scaling effects and facilitate comparison.

8. Materials and methods

8.1. Bioscrubber operation and sampling procedures

Achromobacter xylosoxidans Y234, was cultivated and prepared for inoculation using methods and media that have been previously described [10]. All experiments were conducted using a 6 L New Brunswick BioFlo Trade Mark III bioreactor with a 3 L total liquid working volume. Additional details and an illustration of the experimental apparatus of the TPPB can be found in Nielsen et al. [10]. Nominal operating conditions of the TPPB include an organic volume fraction of 0.33, pH 6.6, a constant temperature of 30 °C, agitation at 800 rpm, and aeration at 60 L/h. However, agitation and aeration rates, as well as the organic fraction, were varied from their nominal conditions as required in order to identify their potential effect on various parameters.

To generate an appropriate model for cell growth, the growth kinetics of *A. xylosoxidans* Y234 on benzene were investigated in a well-mixed, closed batch bioreactor with all orifices being sealed with Teflon septa, containing 3 L of aqueous medium to eliminate stripping losses in a manner similar to that of Monero et al. [30]. Inoculum was pre-adapted for benzene degradation in a 1 L aqueous bioscrubber which was continuously sparged with a dilute benzene gas feed stream for 3 days. Since aeration of the closed batch experiments was not possible, the bioreactors were saturated with 1 atm of pure oxygen before inoculation. Prior to sealing, a desired amount of liquid benzene (0.5–1 mL) and harvested cells (~0.5 g) were added to the closed batch bioreactor to achieve appropriate initial conditions. Aqueous benzene concentrations were determined by assuming a Henry's Law equilibrium relationship with headspace gas concentrations which were quantified by gas chromatography. Liquid samples were used to quantify biomass levels using optical density measurements. Intermittently, aqueous benzene concentrations were also measured by gas chromatography in order to validate the assumed equilibrium relationship with the head space. Sampling was continued until neither head space benzene nor growth was detected. The resulting data were fit to the most appropriate empirical model in order to obtain the associated sets of best-fit parameter estimates via non-linear regression.

Benzene absorption experiments for each phase were separately conducted using 3 L of either aqueous medium or *n*-hexadecane to measure the mass transfer coefficients, $k_L a_{SA}$ and $k_L a_{SO}$ under various operating conditions. The bioreactor was sparged with a gas containing a constant concentration of benzene while monitoring the liquid phase and off-gas for VOC content until the influent and effluent gas concentrations became equal, indicating that equilibrium had been attained.

8.2. Analytical techniques

Gaseous and organic benzene concentrations were directly determined by GC-FID using the methods previously described [10]. Aqueous benzene concentrations were determined by mass balance after extraction with, and GC-FID analysis of, *n*-hexadecane. Biomass concentrations were quantified using optical density measurements and compared to cell dry weight calibrations as previously discussed [10]. Dissolved oxygen concentrations were measured using a polarographic membrane dissolved oxygen probe.

8.3. Numerical methods

Solution of the proposed model, as well as the dynamic sensitivity equations, was performed using Matlab® and the intrinsic ordinary differential equation solver *ode15s*. Model parameters were estimated using linear or non-linear least-squares regression analysis, where appropriate. Non-linear least-squares regression was performed by the Gauss–Newton method as implemented using the intrinsic Matlab® function *nlinfit*.

9. Results and discussion

Estimates for a number of important model parameters were obtained through our preliminary studies, including those related to biphasic oxygen absorption [22], substrate consumption and utilization [10], and phase equilibrium [12]. For the remaining parameters, experiments were designed under selected conditions to allow the model parameters to be individually estimated, preserving their physical interpretation.

9.1. Substrate absorption

The benzene absorption mass transfer coefficients, $k_L a_{SA}$ and $k_L a_{SO}$, were individually estimated for both aqueous medium and *n*-hexadecane, and are presented in Table 1. All data sets followed the anticipated first-order trend and parameter estimates for each phase ($i = A, O$) were obtained by least-squares regression of the linear solution to the following differential

Table 1
Experimentally measured and theoretical values of $k_L a_{Si}$ for the aqueous medium and *n*-hexadecane at various operating conditions in cell-free, single-phase bioscrubbers

Liquid phase	Q_G, N, S_G^{in} (L/h, rpm, mg/L)	$k_L a_{Si}$ (h^{-1})	$Q_G/V_i H_{Si}$ (h^{-1})
Aqueous ($i = A$)	60, 800, 5.7	6.4 ± 0.2	6.5
	120, 800, 9.1	12.4 ± 0.7	13.1
Organic ($i = O$)	60, 800, 22	0.041 ± 0.001	0.04
	120, 800, 9.5	0.083 ± 0.001	0.08

equation describing the material balance on the liquid contents of a single-phase experiment:

$$\frac{dS_i}{dt} = k_L a_{Si}(S_i^* - S_i) \tag{18}$$

The noted disparity between the $k_L a_{Si}$ estimates of the two phases reflects the dissimilarity between their absorption mass transfer resistances, and arises in large part due to differences in fluid properties including equilibrium solubility which can influence the process of surface renewal at the gas–liquid interface [17]. Using the $k_L a_{Si}$ estimates and data from these single-phase absorption experiments, initial rates (where $S_i|_{t=0} = 0$) of dissolved benzene accumulation were also calculated from the data and found to be strongly correlated (results not shown) with the influent gas concentration, since:

$$\left.\frac{dS_i}{dt}\right|_{t=0} \approx k_L a_{Si} \frac{S_G^{in}}{H_{Si}} \tag{19}$$

This observation prompted the use of the following relationship to determine the absorption driving force for each liquid phase, i, in the combined model:

$$S_i^* = \frac{S_G^{in}}{H_{Si}} \tag{20}$$

During these single-phase absorption experiments, effluent gas benzene concentrations were consistently observed to maintain a linear proportionality with the dissolved concentration according to Henry's Law relationships (i.e., $H_{Si} = S_G^{out}/S_i$ for all t). This result is illustrated in Fig. 3, where the slopes of the equilibrium lines equal the Henry's Law coefficients, previously estimated as 0.327 and 0.002 for the aqueous medium and *n*-hexadecane, respectively [12]. This result indicates that
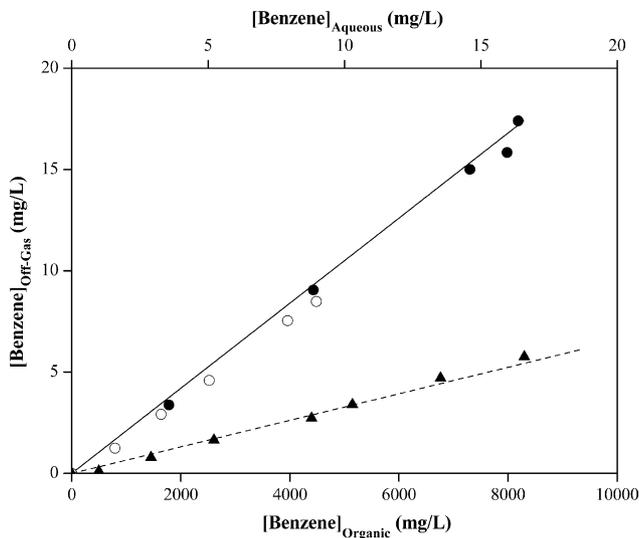

Fig. 3. Comparing dissolved and off-gas benzene concentrations with Henry's Law equilibrium predictions during cell-free, single-phase absorption experiments in aqueous medium (dashed line) and *n*-hexadecane (solid line) under various sets of operating conditions: aqueous medium at 60 L/h, 800 rpm, and $S_G^{in} = 5.8$ mg/L (closed triangles), *n*-hexadecane at 60 L/h, 800 rpm, and $S_G^{in} = 17.5$ mg/L (closed circles), and *n*-hexadecane at 120 L/h, 800 rpm, and $S_G^{in} = 8.9$ mg/L (open circles).

rates of benzene absorption were sufficiently rapid to allow equilibrium to be achieved prior to the gas exiting the bioscrubber. If the simplifying assumptions associated with the original development of Eq. (13) were to remain valid, then it would be analogously true for absorption in the single-phase, i, under otherwise identical operating conditions that:

$$Q_G(S_G^{in} - S_G^{out}) = k_L a_{Si}(S_i^* - S_i)V_T \tag{21}$$

Upon substitution of Eq. (20) and the observed effluent gas equilibrium relationship, Eq. (21) can be re-arranged to predict that $k_L a_{Si}$ will be correlated as:

$$k_L a_{Si} = \frac{Q_G}{V_T} H_{Si} \tag{22}$$

The close agreement between Eq. (22) and the experimental data in Table 1 validates the original simplifying assumptions made regarding substrate absorption and justify the use of Eq. (13) in the combined TPPB model. Other researchers have arrived at correlations similar to Eq. (22) in their respective bioscrubber and bioreactor configurations [31,32]. This simplification implies that mass transfer in this system is very rapid, reaching equilibrium very quickly [31]. In general, however, it is unreasonable to expect that mass transfer will behave in such a manner under all operating regimes, particularly if Q_G is greatly increased, thereby reducing the gas–liquid contact time. Therefore, the general expression of Eq. (12) is preferred and experiments should guide the selection of the most appropriate form of both the mass transfer coefficients and equilibrium driving force, permitting simplifications only where experimentally justifiable.

10. Microbial growth kinetics in closed batch experiments

Although a batch bioreactor may not be ideal for kinetic parameter estimation, the use of preferred continuous culture is unacceptable due to inevitable volatile substrate losses from the open system and their detrimental effect on the material balance. Within a closed batch bioreactor, benzene will equilibrate between the aqueous and head space volumes according to Henry's Law. By using small inoculum sizes, biodegradation rates remained sufficiently slow such that benzene partitioning rates across the gas–liquid interface would likely not limit growth, allowing these phases to be assumed to be in equilibrium. Furthermore, maintenance energy requirements may be neglected from the material balance since their contributions to the total volumetric growth and substrate consumption rates, although still very real, are essentially negligible relative to those growth-associated processes which comprise the majority of the cellular metabolism under these conditions. With these simplifications, the material balances on benzene and biomass can be described by Eqs. (23) and (24).

$$\frac{dS_A}{dt} = -\frac{1}{Y_{X/S}} \frac{\mu X V_T}{(V_A + H_{SA}V_H)} \tag{23}$$

$$\frac{dX}{dt} = \mu X \tag{24}$$

Table 2
Unstructured empirical growth models commonly used for the prediction of the substrate-inhibited microbial kinetics of benzene degradation

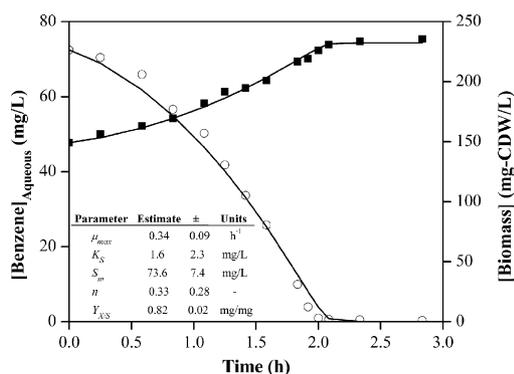| Model structure		References
$\mu = \mu_{max} \dfrac{S_A}{S_A + K_S + (S_A^2/K_1)}$	(25)	[36]
$\mu = \mu_{max} \dfrac{S_A}{S_A + K_S} \left[1 - \dfrac{S_A}{S_m}\right]^n$	(26)	[37]

Fig. 4. Biomass (solid squares) and aqueous benzene (open circles) concentration profiles measured during a single-phase, closed batch experiment with an initial aqueous phase benzene concentration of 75 mg/L. Solid lines represent model predictions using the best-fit parameter estimates (listed in the inset table) of the Luong kinetic model.

Table 3
Summary of the parameter estimates used in the TPPB model

Model parameter	Value	Source
Operating conditions		
S_G^{in} (mg/L)	3	–
C_G^{in} (atm)	0.21	–
Q_G (L/h)	60	–
V_T (L)	3	–
ϕ_{ORG}	0.33	–
Microbial kinetics		
μ_{max} (h^{-1})	0.34	This study
K_S (mg/L)	1.6	This study
S_m (mg/L)	73.6	This study
n	0.33	This study
$Y_{X/S}$ (mg/mg)	0.82	This study
$Y_{X/C}$ (mg/mg)	1.96	[20]
K_C (mg/L)	0.77	[38]
M_S (mg/mg h)	0.0173	[10]
m_S (mg/mg h)	Eq. (1)	This study
m_C (mg/mg h)	0.041	[20]
k_d (h^{-1})	Eq. (2)	This study
Mass transfer		
$k_L a_{CA}$ (h^{-1})	69.9	[22]
$k_L a_{CO}$ (h^{-1})	45.5	[22]
$k_L a_{SA}$ (h^{-1})	6.55	This study
$k_L a_{SO}$ (h^{-1})	0.04	This study
Equilibrium		
H_{CA} (atm L/mg)	0.026	[39]
H_{CO} (atm L/mg)	0.0035	[40]
D_C	7.53	[40]
H_{SA}	0.327	[12]
H_{SO}	0.002	[12]
D_S	163.5	[12]

where V_H is the head space volume in the sealed bioreactor. An appropriate model for μ can then be selected and its associated parameters readily estimated.

The growth kinetics of *A. xylosoxidans* Y234 on benzene was anticipated to follow a substrate inhibited pattern. In previous bioreactor studies, benzene-inhibited kinetics have typically been sufficiently modeled using either Andrews [30,33,34] or Luong [35] kinetics, presented in Table 2. Preliminary experiments indicated that the growth of *A. xylosoxidans* Y234 became completely inhibited at elevated levels of S_A, an observation that is consistent with Luong model predictions. For instance, essentially negligible rates of growth and substrate consumption were observed when initial aqueous benzene concentrations were 400, 235, and 100 mg/L (data not shown). At an initial benzene concentration of approximately 75 mg/L, however, growth occurred and benzene was completely consumed within 2.3 h, as can be seen in Fig. 4. From these data, the best-fit parameters of the Luong model for benzene degradation by *A. xylosoxidans* Y234 in single-phase culture were estimated by non-linear least-squares regression, and are reported in Fig. 4.

11. Parametric sensitivity analysis

Parametric sensitivity analysis was used to investigate which of the parameters each of the predicted responses are most sensitive and when: during transient periods, at steady-state, or throughout the entire simulation. These results will help to dis-

cover how the intentional manipulation of parameters through selection of different materials, microorganisms, or operating conditions can improve performance and identify potentially useful design variables. Although it is the influence of the parameters on S_G^{out} that is of primary interest for enhancing VOC elimination, valuable process information can also be obtained by investigating the sensitivities of the other modeled variables.

The TPPB was simulated under constant operating conditions from start-up through steady state. An organic phase volume fraction of 0.33 and a benzene concentration of 3 mg/L fed at 60 L/h were selected, which is similar to past conditions [12]. The corresponding parameter estimates are listed in Table 3. Since interpretation of the sensitivity results is best performed in reference to the predicted responses themselves, they are plotted in Fig. 5. These predictions will be validated using experimental data in Part II of this work. Although all of the dynamic sensitivity coefficients were calculated and analyzed, only the most pertinent results have been plotted in Fig. 6 for discussion. Note that because of the assumption of spontaneous liquid–liquid partitioning, the behavior of the sensitivity coefficients of S_O and C_O will be analogous to that of S_A and C_A, respectively, and were therefore not reported. It is clear that the influence of many of the parameters were transitory in nature, exerting their effect on the predictions only briefly after start-up and becoming less influential as steady state was approached, or vice versa. The
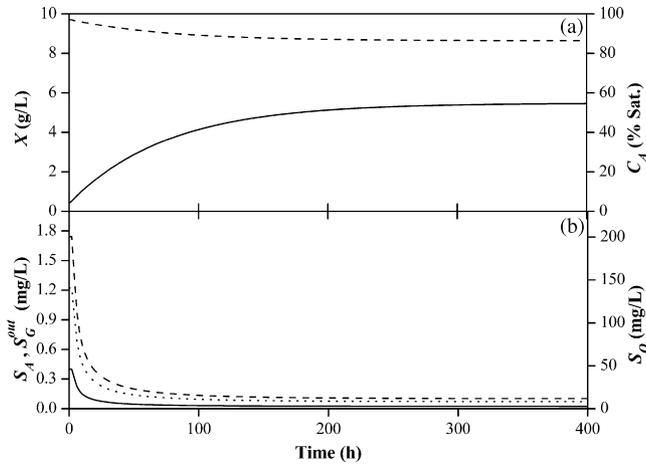
Fig. 5. Simulation of start-up through steady-state operation of a TPPB treating 3 mg/L of benzene in a waste gas fed at 60 L/h with organic phase volume fraction of 0.33, with respect to the model parameters of (a) biomass (solid line), dissolved oxygen (dashed line), and dissolved benzene concentrations in the (b) organic phase (dashed line), aqueous phase (dotted line), and effluent gas (solid line).

predicted response of the models cellular and physical processes to perturbations in the parameter values varied depending upon the state of the system, which initially was not under substrate limiting conditions since the TPPB contained an abundance of dissolved substrate. Since high dissolved substrate concentrations will also occur in response to transient fluctuations, it is expected that those parameters which most greatly impact predicted responses during the initial transitory period will also be the most relevant during transient operation.

Accumulation of biomass in the TPPB equips it with a progressively increasing biocatalytic potential. As steady state is approached, the maximum potential benzene biodegradation rate increases relative to the loading rate, essentially leading to benzene consumption immediately following absorption, thus reducing dissolved substrate concentrations to minimal levels. With the capacity to consume benzene far exceeding its steady-
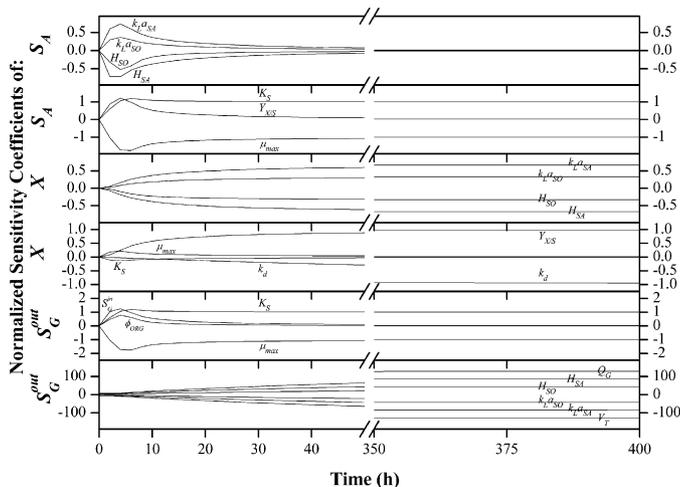

Fig. 6. A selection of the most significant normalized sensitivity coefficient profiles predicted for the proposed model, corresponding to the simulated operation of the TPPB from start-up through steady-state, as shown in Fig. 5.

state supply rate, the result is a desensitization of S_A and S_O to perturbations in the VOC mass transfer parameters (i.e., $k_L a_{Si}$ and H_{Si} values) which translates into performance stabilization during transient fluctuations, as has been previously observed experimentally [12]. Apart from the initial start-up period, the TPPB is predicted to operate at very dilute concentrations of S_A. As such, the process approaches starvation conditions which means that the predicted effect of endogenous metabolism on X (incorporated in Eq. (2)) becomes increasingly important. Under dilute conditions, the substrate affinity of the microorganisms is governed by the values of μ_{max} and K_S, resulting in a high sensitivity of S_A to these parameters. The model was insensitive to the parameters used to describe the inhibitory effect of the substrate in the Luong kinetic model (S_m and n) for the simulated conditions because only dilute concentrations were predicted. C_A was found to be sensitive to the parameters associated with the substrate and oxygen absorption processes, while being relatively insensitive to the biological kinetic parameters due to its high abundance under the conditions studied.

S_G^{out} most strongly depended upon the mass transfer parameters and its predictions were particularly influenced by the properties of the organic phase (H_{SO} and $k_L a_{SO}$). The high sensitivity of S_G^{out} to H_{SA} is consistent with other similar studies [41], and indicates that VOC removal will be greater in water for compounds with lower Henry's Law coefficients. S_G^{out} was also quite sensitive to the microbial kinetic parameters μ_{max} and K_S because these parameters indirectly affect VOC absorption rates through the driving force by establishing a minimum dissolved substrate concentration below which the substrate is not effectively degraded. To achieve high VOC removal rates and efficiencies, the minimum residual dissolved substrate concentration should be substantially different than the equilibrium dissolved substrate concentration, a condition that will be satisfied when $S_A^* \gg K_S$. It is notable that predictions of S_G^{out} are sensitive to variations in ϕ_{ORG} only initially when a significant amount of dissolved substrate is present, but not at steady state. Therefore, it is predicted that ϕ_{ORG} may actually have little effect on S_G^{out} during steady-state operation, however, having a larger organic phase fraction will have a positive effect during transient operation. Finally, Q_G and V_T greatly impact S_G^{out} predictions in equal, yet opposite ways. Higher Q_G and lower total V_T both lead to higher S_G^{out} due to the associated decreases imposed on the gas–liquid contact time. A similar sensitivity to the gas–liquid contact time was also previously reported for a single-phase bioscrubber [42].

The sensitivity analysis has identified a few parameters whose values may be most easily manipulated to yield a significant reduction in S_G^{out}. As a property of the organic phase, H_{SO} can be varied through the selection of alternative second-phases. By minimizing H_{SO} to promote a larger driving force, higher absorption rates can be achieved and S_G^{out} can be reduced at all times. Although $k_L a_{SO}$ is not an inherent property of the organic phase compound, the physical properties of the selected phase can influence the mass transfer coefficient [43]. Alternatively, the results predict that performance can be enhanced by selection of an alternative biocatalyst whose kinetic parameters μ_{max} and K_S are maximized and minimized, respectively. The particular

sensitivity of the TPPB model to μ_{max} and K_S estimates is also shared by biofilters [44]. Oligotrophs, or microorganisms that are capable of growth at very low substrate concentrations [45], would therefore be ideal biocatalysts in the TPPB.

12. Conclusion

A mechanistic model of a TPPB process used to remove and degrade VOCs from waste gases has been presented. Experimentation has been performed to isolate the relevant and characteristic parameter estimates required to simulate the biodegradation of benzene by *A. xylosoxidans* Y234 using *n*-hexadecane as the organic phase. Parametric sensitivity analysis has been used to study the effect of the parameter estimates on the model predictions, as well as to identify potential design parameters whose manipulation could most easily lead to improved performance and reduced effluent gas VOC concentrations. H_{SO}, μ_{max} and K_S are predicted to have the greatest effect under all conditions, while ϕ_{ORG} is expected to be of particular importance during transient operation of the TPPB. The predicted influence of these parameters will be further explored in Part II of this manuscript, following validation of the model using steady-state and dynamic data to assess the accuracy of its predictions. These results will be investigated in further detail in Part II in order to develop useful criteria for TPPB design and study their performance potential, particularly under transient conditions.

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