

A Strategic Approach for the Design and Operation of Two-Phase Partitioning Bioscrubbers for the Treatment of Volatile Organic Compounds

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*A strategic approach for the design of two-phase partitioning bioscrubbers (TPPBs) has been formulated using, as a basis, a re-evaluation of extensive literature data available for the degradation of benzene by Achromobacter xylosoxidans Y234 in TPPBs with n-hexadecane as the partitioning phase. Using a previously determined maintenance coefficient for benzene, we determined that an inlet benzene loading rate of 100 mg/h requires 5,928 mg cell mass at biological steady state and 243.0 mg O₂/h. The total oxygen-transfer rates (TOTRs) into the TPPB increased by 83.5% with 33.3% of organic phase compared with a single aqueous phase and were significantly influenced by gas flow rate, whereas agitation has a minor affect. The fraction of organic phase used was suggested to be the primary parameter with which the TOTR into the TPPB may be altered. Although the presence of an organic solvent in the TPPB remarkably increased the TOTR, the total benzene transfer rate into the TPPB remained largely insensitive due to the intrinsic low Henry's law constant (or relatively high solubility) of benzene in water. Finally, we have integrated the elements of this analysis into a set of heuristic criteria that can serve as a guideline for the design of TPPB systems for future volatile organic compound treatment applications. © 2010 American Institute of Chemical Engineers *Biotechnol. Prog.*, 26: 1777–1786, 2010*
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Introduction

Aromatic volatile organic compounds (VOCs) such as benzene, toluene, and xylene (BTX) are major products of the petroleum and fine chemical industries and are among the most frequently used organic solvents.¹ Because of their toxic and/or carcinogenic nature, their release into the environment is strictly controlled as priority environmental pollutants by the U.S. Environmental Protection Agency.¹ Although present as airborne contaminants, these compounds also frequently enter soil, sediments and groundwater due to leakage from underground storage tanks, pipelines, and accidental spills.² Of the biotechnologies used for the treatment of VOCs, biofiltration has been shown to be useful because of its uncomplicated and inexpensive design which is typically coupled with long-term performance requiring only minimal maintenance and operator attention.³ However, biofilters have great difficulty in dealing with high inlet VOC concentrations because of the potential for microorganisms to be inhibited or killed at the biofilter inlet,⁴ and are also prone to clogging and channeling.

As an alternative, two-phase partitioning bioreactors have successfully been applied to the treatment of high concentrations of pollutants⁵ and were originally designed as a novel device attached to a bubble column for capturing gaseous benzene.¹ However, the first design of this type of system required considerable operator intervention to maintain two distinct liquid phases and to operate the system at steady state. Design improvements led to the two-phase partitioning bioscrubber (TPPB) in which aqueous and organic phases are homogeneously mixed,⁶ and we have demonstrated the practical application of TPPB technology to the treatment of VOCs, in particular benzene,^{3,7,8} with some publications directed to the demonstration of process feasibility^{3,6,7} and others toward fundamental issues, such as maintenance energy and oxygen transfer.^{7,9} Recently, TPPBs have also been applied to the treatment of other pollutants such as styrene,¹⁰ isopropylbenzene,¹¹ dichloromethane,¹² pentachlorophenol,¹³ *n*-hexane,¹⁴ and mixtures of up to 11 compounds.¹⁵ Silicone oils have been widely used as an organic phase,^{10–12,14} although other solvents such as cutting oil¹⁵ and dioctyl sebacate¹³ have also been used. So far, however, there has been no general strategy suggested for the design of the TPPB involving, inter alia, solvent selection, cell mass requirements, and key operating

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parameters. Moreover, it is first necessary to determine whether a TPPB will provide sufficient performance advantages over a single aqueous phase system, or biofilter, to rationalize the potentially higher capital costs associated with this technology, notwithstanding the additional advantages of TPPBs such as buffering for fluctuating VOC concentrations and prevention of VOC air-stripping to the environment.^{1,16}

Using data from a number of our previous publications, we now provide a supplemental analysis of important fundamental relationships involved in the operation of TPPBs, which are essential for its satisfactory performance. In addition, we also consider the important lessons learned in many other available references to generate a set of heuristic criteria which can be used by those interested in designing and operating TPPBs for VOC removal.

Materials and Methods

Experimental conditions

The importance of the cellular maintenance coefficient has been suggested in a previous study.⁷ *Achromobacter xylosoxidans* Y234 was used to degrade benzene. The TPPB consisted of a 5 L bioreactor (New Brunswick, BioFlo III, USA) with 3 L working volume, agitated with two Rushton turbines at 30°C. *n*-Hexadecane was used as the sequestering phase in the TPPB. The other experimental conditions were described in the same paper. The data regarding oxygen transfer in the TPPB were adapted from the papers by Nielsen et al.^{8,9,17}

Theoretical background

Oxygen Transfer into the TPPB. When instantaneous partitioning of dissolved oxygen (DO) between the aqueous and organic phases can be assumed, it was previously suggested that the oxygen transfer rate (OTR) into the aqueous phase can be modeled as⁹:

$$\frac{dC_{O-A}}{dt} = \left(\frac{k_L a_A V_A + k_L a_O D_{OA} V_O}{V_A + D_{OA} V_O} \right) (C_{O-A}^* - C_{O-A}) = k_L a_{TPPB} (C_{O-A}^* - C_{O-A}) \quad (1)$$

where C_{O-A} , C_{O-A}^* , D_{OA} , $k_L a_A$, and $k_L a_O$ represent oxygen concentrations (mg/L) and saturated oxygen concentrations (mg/L) in the aqueous phases, partition coefficient of oxygen between organic and aqueous phases and oxygen transfer coefficients (1/h) in the aqueous and organic phases, respectively. V_A and V_O represent the volumes of aqueous and organic phases, respectively. The equilibrium partition coefficient of oxygen between *n*-hexadecane and water was given as 7.53 at 30°C.¹⁸ This equation indicates that the OTR coefficient into the aqueous phase in the TPPB ($k_L a_{TPPB}$) depends on the OTR coefficients measured in each single phase, the volume of each phase and partition coefficient of oxygen between the two phases. In a similar manner, we can also derive an equation regarding the OTR into the organic phase in a TPPB:

$$\frac{dC_{O-O}}{dt} = k_L a_{TPPB} (C_{O-O}^* - C_{O-O}) = k_L a_{TPPB} D_{OA} (C_{O-A}^* - C_{O-A}) \quad (2)$$

where C_{O-O} and C_{O-A}^* represent oxygen concentrations (mg/L) and saturated oxygen concentration (mg/L) in the organic

phases. Together, Eqs. 1 and 2 indicate how several different parameters can influence oxygen transfer in the TPPB. Because the two phases are completely mixed and instantaneous partitioning of oxygen between the two phases is assumed, there is only one OTR coefficient controlling oxygen transfer into the TPPB, $k_L a_{TPPB}$ here. The total oxygen-transfer rate (TOTR) is the sum of those into each phase. By multiplying each volume of aqueous and organic phases in Eq. 1 or 2, the TOTR into the TPPB can be calculated as:

$$\text{TOTR}_{TPPB} = (k_L a_{TPPB} V_A + k_L a_{TPPB} D_{OA} V_O) \times (C_{O-A}^* - C_{O-A}) \quad (3)$$

By substituting $k_L a_{TPPB}$ with the original combined terms in Eq. 1, Eq. 3 is rearranged as:

$$\text{TOTR}_{TPPB} = k_L a_A V_A (C_{O-A}^* - C_{O-A}) + k_L a_O V_O (C_{O-O}^* - C_{O-O}) \quad (4)$$

This equation, which can be expected intuitively by the assumption of instantaneous equilibrium of oxygen between the two phases, can be said to be a homogenous mass-transfer model with weighted average mass-transfer rate. Thus, if TOTR itself is the only concern, Eq. 4 can be alternatively used.

If we then set the total working volume and the portion of organic phase (POP) as V_T and Φ , respectively, Eq. 3 becomes:

$$\text{TOTR}_{TPPB} = \{k_L a_{TPPB} + k_L a_{TPPB} \Phi (D_{OA} - 1)\} \times (C_{O-A}^* - C_{O-A}) V_T \quad (5)$$

$$k_L a_{TPPB} = \frac{k_L a_A (1 - \Phi) + k_L a_O D_{OA} \Phi}{(1 - \Phi) + D_{OA} \Phi} \quad (6)$$

It follows that the theoretical maximum OTR is achieved when the oxygen concentration in the aqueous phase is zero ($C_{O-A} = 0$). Under these conditions,

$$\text{TOTR}_{TPPB, \max} = (k_L a_{TPPB} V_A + k_L a_{TPPB} D_{OA} V_O) (C_{O-A}^*) \quad (7)$$

or

$$\text{TOTR}_{TPPB, \max} = \{k_L a_{TPPB} + k_L a_{TPPB} \Phi (D_{OA} - 1)\} \times (C_{O-A}^*) V_T \quad (8)$$

Results and Discussion

Our previous studies have demonstrated that TPPBs display a unique phenomenon, a biological steady state, which arises due to the maintenance requirements of the cells and is characterized by no increase in cell mass, even over prolonged periods of continuous substrate feeding. In addition, many researchers have considered oxygen transfer to be one of the most important beneficial effects of the use of organic solvents in TPPBs, often referring to them as "oxygen vectors."^{10,19} Any enhancement of oxygen transfer via the use of organic solvents would be offset by the oxygen demand, which is proportionally dependent on the cell mass within the TPPB. Therefore, our analysis begins with an examination of

the cell mass at biological steady state for the treatment of a VOC at a given loading rate, leading to an examination of the oxygen requirement of a TPPB system, and ultimately to the impact of organic phase fraction on TPPB performance.

Cell mass required for the treatment of a benzene loading rate

In designing TPPBs, it is important to determine the minimum cell mass required to provide sufficient biocatalytic activity such that the target pollutant can be degraded at a rate that is greater than or equal to the rate at which it is fed. Although the maintenance coefficient is variable during TPPB operation,²⁰ it converges to a specific value at biological steady state where there is no observed net increase in cell mass as most of the substrate supplied is used in support of the maintenance requirements of the cells with negligible changes to the aqueous and organic substrate concentrations.⁷ Under this condition, the following equation can be used to estimate the maintenance coefficient.^{7,20}

$$m = \frac{F(C_i - C_f)}{V_A X_A} \quad (9)$$

where F , C_i , C_f , X_A , and m represent gas flow rate (L/h), inlet and outlet gaseous benzene concentrations (mg/L), cell mass (mg/L), and maintenance coefficient (mg benzene/mg cell/h), respectively. As was demonstrated previously, experimental estimates of the maintenance coefficient (measured at biological steady state) were found to be constant, irrespective of the benzene loading rate (BLR) to the TPPB.⁷ The maintenance coefficient relates the minimum rate at which substrate must be consumed to fully support the essential (maintenance) functions of a given mass of cells.²¹ A high-maintenance coefficient implies that a smaller mass of cells is required and maintained at biological steady state. From the view point of cell mass requirements, cells with high-maintenance coefficient would be preferred in TPPBs because a lower cell mass would correspond to less medium, waste biomass production, a smaller working volume requirement, and lower overall operating costs.

From Eq. 9, we can derive a relationship between maintenance coefficient, cell mass, and VOC removal efficiency (R)

$$X_A = \frac{FC_i R}{mV_A} \quad (10)$$

The value of m was previously calculated to be $1.67 \times 10^{-2} \text{ h}^{-1}$,⁷ and we set the removal efficiency to be 0.99 (indicative of previously demonstrated performance levels). Because the volume of the aqueous phase is prescribed by the system design, the cell mass requirement at biological steady state is then a function of FC_i , the BLR. All the known values can be put into Eq. 10 resulting in:

$$X_A = \frac{59.28FC_i}{V_A} \quad (11)$$

This relationship implies that the cell mass required at biological steady state is linearly correlated with the inlet benzene concentration, as long as the gas flow rate, the volume of aqueous phase, and the removal efficiency all remain constant. This result further implies that a TPPB could theoretically treat gas streams with even higher benzene concentrations by increasing its biomass content. Self-regulation of biomass

levels is a substantial design advantage of the TPPB and is feasible provided that there exist no other growth-limiting factors, such as the depletion of essential medium components or an insufficient supply of DO. Accordingly, the possibility of oxygen limitation under various operating conditions has been examined and the results are presented in the next section.

Oxygen-transfer rate required to avoid oxygen limitation

Theoretical Maximum Benzene Loading Rate. In the design and operation of TPPBs, the carbon source (e.g., benzene) should be the only growth limiting factor. Another plausible limiting factor, particularly in cultures with a high-cell density, could be DO. The specific oxygen consumption rate of *A. xylooxidans* Y234 growing on benzene at biological steady state in a TPPB was given as $0.041 \pm 0.008 \text{ mg O}_2/\text{mg cell/h}$.¹⁷ Therefore, we can make the following inference at biological steady state:

Inlet benzene mass-loading rate (100 mg/h) \rightarrow cell mass required (5,928 mg) \rightarrow oxygen-transfer rate required (243.0 mg O₂/h).

Accordingly, we can suggest following relationship:

$$\text{TOTR}_{\text{TPPB}} = 2.43FC_i \quad (12)$$

In terms of carbon balance, if there is no cell growth at the biological steady state, benzene should be completely oxidized to generate maximum energy, which requires 3.1 mg of oxygen per mg of benzene according to stoichiometric calculations. The inconsistency implies that 21.6% of the carbon of benzene was used for other purposes such as cell growth, intermediate production, storage materials, etc. If the maximum value, 0.049 mg O₂/mg cell/h, is taken, the inconsistency becomes as low as 6.3%. Along with the remarkably reduced uptake rate of nitrogen during biological steady state,⁸ these results may indicate that minor cell growth and death occurs during the biological steady state because no discernable dead cell accumulation was observed during this stage.^{7,8} The OTR in Eq. 12 is representative of the aqueous phase where the cells reside. However, because it can be assumed that partitioning equilibrium of DO between the two phases occurs instantaneously based on the oxygen demand by the cells, TOTR available by the microorganisms is the sum of the OTRs to both phases. To calculate TOTR, $k_L a_{\text{TPPB}}$ is first calculated using Eq. 6 with $k_L a_A$ and $k_L a_O$ measured previously.⁹ As Figure 1 indicates, $k_L a_{\text{TPPB}}$ decreases as the POP increases, which was also experimentally confirmed.²² The result is reflected by the fact that the OTR coefficient into a single organic phase is much smaller than that in a single aqueous phase.⁹ Although some researchers reported that the addition of hydrocarbons such as *n*-dodecane and *n*-hexadecane increased the mass-transfer coefficient of oxygen,^{23,24} there is no general rule for the effect of hydrocarbon addition on the coefficient, that is, it could increase steadily, initially increase but subsequently decrease over critical POP or not change with increasing POP.^{25,26} The reason for the decrease in mass-transfer coefficient over POP is separately considered in the aspect of the specific interface area, a , and liquid-film mass-transfer coefficient, k_L , respectively. In this system, agitation is high enough to make the liquid phase completely homogenous and gas bubbles dispersed. The increase of POP could promote the coalescence of bubbles, as in the case of silicone

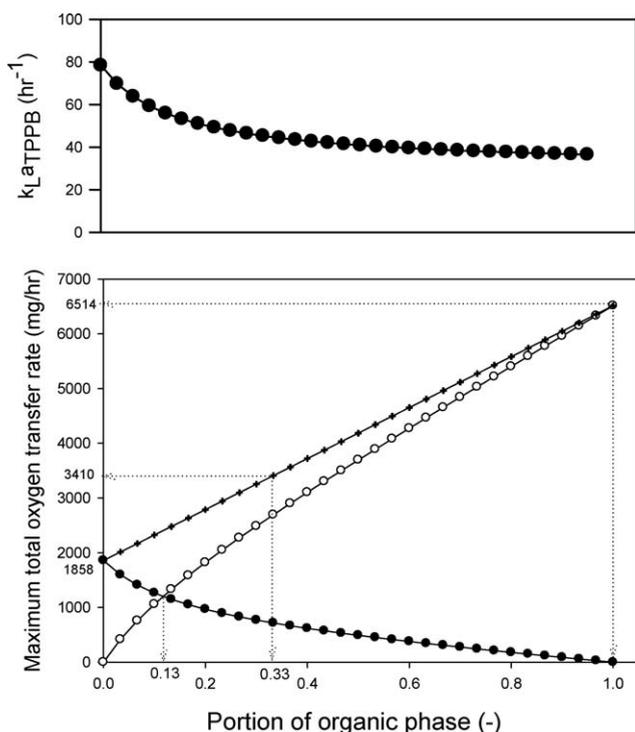


Figure 1. The maximum oxygen transfer rate into the aqueous and organic phases in the TPPB with 3 L of working volume.

Top: Effect of portion of organic phase on the oxygen transfer rate coefficient into the TPPB. Bottom: ●, oxygen transfer rate into aqueous phase; ○, oxygen transfer rate into organic phase; +, total oxygen transfer rate into the TPPB. The aeration rate and agitation speed are 60 L/h and 800 rpm, respectively.

oil.¹⁰ Other researchers reported that only a 15% increase in a was observed with 23% of *n*-dodecaene,²⁶ which would be a minor contribution to the mass-transfer rate coefficient. In contrast, k_L is believed to be greatly affected by POP. The negative effect of the organic solvent, *n*-hexadecane, on OTR coefficient may be due to an increase in the apparent viscosity of the liquid phase, which has a negative effect on oxygen transfer.²⁷ Other researchers have also explained this effect in terms of the adsorption of organic liquid droplets at the air–aqueous medium interface forming a rigid film, which in turn causes resistance to oxygen transfer through the air–liquid interface.^{23,28,29}

With Eqs. 5–8, the theoretical maximum OTR into each phase of the TPPB at 60 L/h of aeration rate and 800 rpm was calculated, and is also shown in Figure 1. These predictions indicate that as the POP increases so too does the maximum TOTR. Despite lower values of $k_L a_{\text{TPPB}}$, increases in TOTR resulting from the addition of *n*-hexadecane are due to increases in the mass-transfer driving force ($C_{O-O}^* - C_{O-O}$), or $D_{OA}(C_{O-A}^* - C_{O-A})$. When POP is ~0.13, the OTRs into each phase are nearly equal, whereas at a POP of 0.33, or 2 L aqueous and 1 L organic phases, TOTR is ~3,410 mg/h. As extreme cases, the maximum TOTRs into a single aqueous and an organic phase are 1,858 and 6,514 mg/h, respectively. These values would imply that the TPPB could treat a BLR as high as 765 and 2,681 mg/h, respectively, which under the same operating conditions correspond to inlet benzene concentrations of 12.8 and 44.7 mg/L. Of course, these values are simply of theoretical interest as cells would not be expected to survive in a pure organic phase, nor under absolute oxygen deficiency.

Effect of Operating Conditions on Oxygen-Transfer Rate. In this section, we investigate the effect of the aeration and agitation rates on the OTR in the TPPB. Because benzene is fed as a gaseous phase, aeration serves as the delivery medium of not only benzene but also of oxygen. The precondition of this investigation is that less than 1% of the loaded benzene escapes from the TPPB without being captured by the liquid phase because of the high affinity of *n*-hexadecane for benzene, infinite solubility and a partition coefficient of 140.1 of benzene between the two phases,³⁰ and large interfacial area that exists between the two, well-mixed phases. The absorption rate of benzene into the TPPB will be discussed in detail in section Determining the portion of organic phase. As suggested in Eq. 6, $k_L a_{\text{TPPB}}$ at constant aeration and agitation is determined by the OTR coefficients into each phase, POP, and the partitioning coefficient of oxygen between the two phases. The OTR coefficient at constant aeration and agitation rates can be expressed as.³¹

$$k_L a = \alpha \left(\frac{P_g}{V} \right)^\beta (v_s)^\gamma \quad (13)$$

where α , β , and γ represent empirical constants. P_g , V , and v_s represent the power input into the aerated bioreactor, bioreactor working volume, and superficial gas flow rate, respectively. The values of these parameters are characteristic of the bioreactor and mixing conditions employed and should be defined for each application. It should also be noted that power input without aeration, P , is dissipated by aeration, leading to P_g . If we assume that the viscosity and the density of the medium are constant, the power input per volume of medium without aeration, P/V , remains constant. To calculate power dissipation by aeration, the aeration number (N_A), reflecting the effects of aeration and, was calculated for this study for six-bladed Rushton turbines and was found to be in the range of 0.003–0.016. Because power dissipation of the Rushton turbine is not noticeable within the experimental range, we assumed that P_g/V is approximately constant.³¹ Accordingly, Eq. 13 can be simplified to yield the following relationship relating the OTR coefficient at two different values of the superficial flow rate:

$$k_L a_2 = k_L a_1 \left(\frac{v_{s,2}}{v_{s,1}} \right)^\gamma \quad (14)$$

The values of γ were previously given as 0.49 for the aqueous phase and 0.71 for the organic phase (*n*-hexadecane).⁹ When, for example, we double the gas flow rate, the new estimates of the OTR coefficient become 1.40 and 1.64 times higher for a single aqueous and an organic phase, respectively. Alternatively, a decrease of gas flow rate by 50% then decreases the OTR coefficient to 71% and 61% for a single aqueous or organic phase, respectively. These results imply that the OTR coefficient in the organic phase is more susceptible to changes in gas flow rate than is the aqueous phase. Using the data of OTR coefficients for a single aqueous or organic phase,⁹ $k_L a_{\text{TPPB}}$ under various operating conditions were recalculated, and the results now demonstrate that increasing aeration rate significantly enhanced $k_L a_{\text{TPPB}}$ as shown in Table 1. Meanwhile, increasing the agitation rate showed an inverse effect on $k_L a_{\text{TPPB}}$, although its effect was insignificant. Accordingly, agitation of 400 rpm is sufficient for completely mixed conditions.

Although the maximum TOTR is obtained when DO is zero, conservative practice suggests that the minimum DO

Table 1. Total Oxygen-Transfer Rate into the TPPB under Various Aeration and Agitation Conditions

Agitation (rpm)	Oxygen-Transfer Rate (mg-O ₂ /h)		
	Aeration Rate (L/min)		
	1	2	3
400	52.6*	88.8*	113.7*
	1,979 (822.5)	3,343 (1,390)	4,279 (1,779)
600	48.0*	86.5*	114.5*
	1,807 (751.3)	3,255 (1,353)	4,309 (1,791)
800	45.3*	83.5*	110.6*
	1,705 (708.7)	3,142 (1,306)	4,164 (1,730)

* Represents $k_L a_{TPPB}$ and values in parentheses are the maximum benzene loading rate (mg/h) to be treated with 99% removal efficiency. The total oxygen-transfer rate is estimated with the dissolved oxygen level in the aqueous phase being 50% of saturation. These data are for a 5-L bio-reactor with 3-L working volume, 2-L aqueous phase, and 1-L *n*-hexadecane, at 30°C.

level in the aqueous phase should be above 50% of saturation ($C_{O-A} = 0.5 C_{O-A}^*$). The DO level of 50% was selected based on our experience with this system; however, this value can be changed as needed for other microorganisms. With the data of $k_L a_{TPPB}$ in Table 1, TOTR into the TPPB with a working volume of 2 L of aqueous phase and 1 L of organic phase was calculated and also shown in Table 1, along with the maximum BLRs under these operating conditions.

Based on the oxygen requirement at biological steady state, the maximum inlet benzene concentration treatable at 1 L/min aeration and 400 rpm would correspond to 13.7 mg/L (loading rate of 822.5 mg/h). In this case, the total cell mass should be 48,758 mg at biological steady state to achieve 99% removal efficiency. On the other hand, as high as 1,779 mg/h of loading rate or 9.9 mg/L of inlet benzene can be treated under the condition of 3 L/min aeration and 400 rpm. It should be noted that the relationship in Table 1 was established based on maintaining 50% DO saturation. These operating parameters could be loosened (or tightened) according to the dependence of the specific growth rate of cells on the DO level, which could itself be described with a Monod-type equation.³²

Parameter Sensitivity Analysis at Biological Steady State. As stated, because we assume instantaneous partitioning of oxygen between the two phases, it is the TOTR into the TPPB and not the OTR to the aqueous phase alone that should be used as an indicator of potential oxygen-limiting conditions. TOTR can be changed by altering POP, D_{OA} , or the aeration rate. When designing a new TPPB process for the treatment of another VOC, a different organic phase will be likely selected, which will of course possess its own D_{OA} value. Although D_{OA} remains a fixed value for a specific organic solvent, POP and aeration rate may typically be freely manipulated (within physical limitations). To determine which parameter most controls the TOTR at biological steady state, parameter sensitivity analysis was performed by changing the value of each parameter from -95 to 100% and measuring the resultant effect on TOTR predictions. The base case condition for this analysis was set as POP of 0.33, D_{OA} of 7.53, and an aeration rate of 2 L/min. The working volume and agitation speed were fixed at 3 L and 400 rpm, respectively, and the change of OTR coefficient by aeration

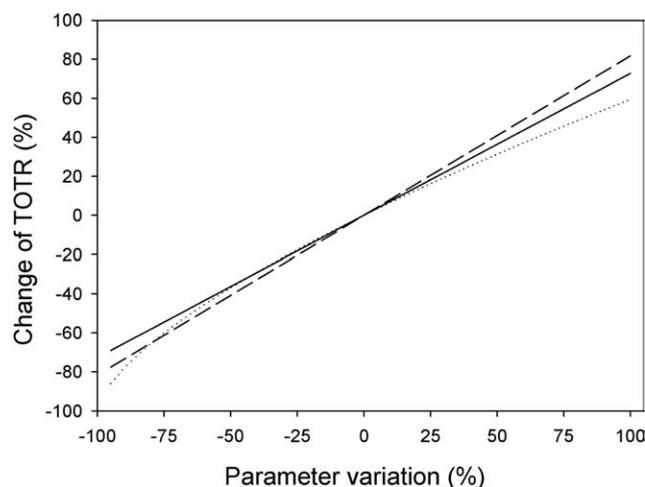


Figure 2. Sensitivity analysis of parameters affecting total oxygen transfer rate into the TPPB.

Solid, dashed and dotted lines represent the change of total oxygen transfer rate by changing POP, D_{OA} , and air-flow rate, respectively.

rate was modeled using Eq. 14. Statistically, there should be three two-variable interactions and one three-variable interaction. Because the aim of this section is to select the major factor out of three variables affecting TOTR, we considered only main variables not interactions. The results indicate that TOTR can be noticeably, and almost equivalently, enhanced by increasing POP, D_{OA} , or aeration rate as shown in Figure 2.

The organic phase serves to enhance the supply of oxygen and of carbon source (VOC) to the TPPB. In fact, the organic solvent is typically selected on the basis of its affinity toward the pollutant of interest,³⁰ rather than to oxygen. Although D_{OA} can be altered by changing temperature in the TPPB, this could affect the partitioning coefficient of the target pollutant and cell viability as well as D_{OA} . However, one should keep in mind that because POP is closely associated with D_{OA} , solvents with a high D_{OA} allow for designs which incorporate less organic solvent, in turn reducing operating costs. Aeration rate can be easily controlled under laboratory conditions, however, in actual VOC applications aeration would be tightly related with the pollutant loading rate and it would not be as easy to alter gas flow rates discharging from industries. Additionally, artificial increases in aeration rate require more energy input on a continuous basis. Therefore, we would expect that there would exist strict limits in our ability to freely manipulate the aeration rate. In contrast, however, POP can be easily changed in the design and operation of most TPPBs. Consequently, it is apparent that POP is the major operating parameter in TPPB designs with which one might control TOTR.

Determining the portion of organic phase

We have shown that POP should serve as the key design and operating parameter in TPPBs. Because the organic phase serves as the primary storage and delivery medium of both oxygen and substrate, it is also necessary to investigate the effects of the addition of organic solvent in the TPPB on their transfer rates. As noted, as POP is increased more oxygen may be transferred into the TPPB. However, because only the aqueous phase can be assumed to be available to support the biomass, the POP should be as small as possible to provide sufficient aqueous volume in the TPPB to sustain

biocatalytic activity, as well as to conserve capital and operating costs. At the same time, POP must also remain sufficiently high such that the minimum oxygen transfer requirements of the cells are met. According to the strategy suggested thus far, the inlet BLR will determine the amount of cell mass at biological steady state, and hence the TOTR into the TPPB. Because TOTR is strongly dependent on the POP, the inlet loading rate can in turn be used for the calculation of POP. As has been observed experimentally,⁷ the inlet loading rates can fluctuate during normal operation. Accordingly, it is necessary to consider the incorporation of a safety factor within the design of TPPBs, which we will conservatively set here to 20%. The following relationship can then be suggested.

$$\text{TOTR}_{\text{required}} = 1.2 \times \text{TOTR} \quad (15)$$

When treating, for example, a gas stream containing 5 mg/L benzene at 120 L/h (equivalent to an inlet loading rate of 600 mg/h), we would predict (by Eq. 12) that a minimum TOTR of $1.2 \times 1,458$, or 1,750 mg O₂/h, would be required. To conserve energy, the agitation rate was set at 400 rpm, which we have found to be sufficient for homogeneity. Under these conditions, the TOTR into a TPPB with 2 L aqueous and 1 L organic phases is 3,343 mg O₂/h, as already shown in Table 1 (where C_{O-A} was set to be 0.5 C_{O-A}^* to avoid oxygen limitation). Because there exists a large margin of 1,593 mg O₂/h (1,750 vs. 3,343 mg O₂/h) between the TOTR and the minimum metabolic requirement, under these conditions we could decrease POP until the TOTR reached this minimum level (1,750 mg O₂/h) by applying Eqs. 5 and 6. In this case, when V_O is 0.35 L, corresponding to a POP of just 0.12, TOTR will become 1,758 mg O₂/h (under similar operating conditions). Therefore, a POP of 0.12 would supply sufficient oxygen to the TPPB. If we then increase the inlet benzene concentration to 10 mg/L with all other parameters remaining constant, a TOTR of $1.2 \times 2,916$ or 3,499 mg O₂/h into the TPPB would be required, which in turn would require 1.07 L of organic phase, or a POP of 0.36, to ensure the supply of 3,514 mg O₂/h. These results imply that higher BLRs correspond to higher POP requirements, which in turn control the TOTR into the TPPB. It should be noted that the DO level of 50% and a safety factor of 20% may be altered as circumstances dictate.

Since *n*-hexadecane has a much higher affinity for benzene than does water, it is believed to prevent gaseous benzene from leaving the TPPB in a manner superior to that of a single aqueous phase.¹ Therefore, most of the benzene can be captured in the TPPB containing *n*-hexadecane, which would be a fundamental precondition for high benzene removal efficiencies. We previously stated that POP should be as small as possible, but low POP values could also reduce the sequestering effect of the solvent. Therefore, it is necessary to again suggest a lower limit of POP at which more than 99% of benzene will be absorbed in the TPPB, which would ensure benzene removal efficiencies of at least 99%. Because the POP should meet the requirements of oxygen and benzene simultaneously, the higher POP value resulting from the two different estimates would serve as the optimum POP.

In an analogous manner to oxygen, the total benzene transfer rate (TBTR) may be calculated as the sum of benzene transfer rates into each phase, as:

$$\text{TBTR} = k_L a_{\text{gas-A}} (C_A^* - C_A) V_A + k_L a_{\text{gas-O}} (C_O^* - C_O) V_O \quad (16)$$

where $k_L a_{\text{gas-A}}$ and $k_L a_{\text{gas-O}}$ represent benzene transfer rate coefficients from the gas phase into each of the aqueous and organic phases, respectively. These coefficients were found to increase in proportion to the superficial gas flow rate but remained independent of inlet benzene concentration.^{1,32} These coefficients were also found to be expressed “approximately” as FH_A/V_T and FH_O/V_T for the aqueous and organic phases, respectively, under the conditions for which a constant gas hold-up, rapid change of entrained gaseous benzene concentration from its inlet to its exit conditions (i.e., a high-mass-transfer rate which allows equilibrium to be rapidly established) can all be assumed.³² H_A and H_O are Henry’s law constants of a VOC, in this case benzene, for the aqueous and organic phases, respectively. High Henry’s law constants generally translate into low solubility of a solute in a solvent, resulting in the compound being readily stripped from that phase. At equilibrium, C_A^* and C_O^* may be approximated as C_i/H_A and C_i/H_O for the aqueous and organic phases, respectively, under the same set of assumptions stated above.³² Using these approximate relationships, the TBTR into the TPPB can then be expressed as:

$$\text{TBTR} = FH_A \left(\frac{C_i}{H_A} - C_A \right) V_A / V_T + FH_O \left(\frac{C_i}{H_O} - C_O \right) V_O / V_T \quad (17)$$

When working with dilute solutions of nonpolar substance and where instantaneous equilibrium can be assumed, the following relationship may be derived.

$$C_O = P_{O-A} C_A = \frac{H_A}{H_O} C_A \quad (18)$$

Where P_{O-A} is the partition coefficient of benzene between aqueous and organic phases. Accordingly, Eq. 17 leads to

$$\text{TBTR} = FH_A \left(\frac{C_i}{H_A} - \frac{H_A C_A}{H_A} \right) V_A / V_T + FH_O \left(\frac{C_i}{H_O} - \frac{H_A C_A}{H_O} \right) V_O / V_T \quad (19)$$

or,

$$\text{TBTR} = F(C_i - H_A C_A) V_A / V_T + F(C_i - H_A C_A) V_O / V_T = F(C_i - H_A C_A) \quad (20)$$

Interestingly, Eq. 20 indicates that the volumetric mass-transfer rate of benzene into the organic phase is identical to that into the aqueous phase, implying that the TBTR is independent of POP. In other words, the performance of a single, aqueous bioscrubber is equivalent to that of a biphasic, TPPB for the treatment of benzene in the range of conditions examined. Although these results appear to contradict our original expectations, this result was also previously demonstrated experimentally¹⁷ where 98.7% removal efficiency was achieved using the TPPB containing only a single aqueous phase fed with 9.9 mg/L benzene at 90 L/h gas flow rate. Moreover, a similar conclusion was also drawn from a simulation study^{32,33} where POP was predicted to return only a modest improvement on steady state performance of the TPPB. The reason behind this phenomenon will be discussed in greater detail below.

To determine the degree of absorption of benzene quantitatively, the absorption efficiency of benzene is defined by the total benzene absorption rate divided by BLR, as:

$$\text{Absorption efficiency} = \frac{F(C_i - H_A C_A)}{F C_i} = 1 - \frac{H_A C_A}{C_i} \quad (21)$$

In a system in which the exhaust gas is at equilibrium with the benzene concentration in the aqueous phase, $H_A C_A$ becomes equivalent to C_f . Because H_A and C_A are constant at 0.327 and ~ 0.05 mg/L when treating 5.5 mg/L or 9.2 mg/L of inlet benzene at 60 L/h,^{7,32} the absorption efficiencies for the each case are 99.7% and 99.8%, respectively. The remaining benzene (~ 0.2 – 0.3%) represents that portion which is stripped from the TPPB by gas flow. Therefore, the theoretical maximum removal efficiencies of the TPPB for these cases are $\sim 99.7\%$ when all the benzene absorbed is consumed by the cells.

Because the Henry's law constant depends on the type of solute and solvent, as well as the operating temperature, it can be treated as a constant here. C_A , on the other hand, may be influenced by multiple factors, including the inlet BLR, benzene transfer rate into each phase, and the benzene biodegradation rate. According to a previous study,³² the removal efficiency of benzene in the TPPB was noticeably influenced by the values of μ_{\max} and K_s , parameters which are characteristic of the selected biocatalyst. However, because TPPBs have typically been operated under mass-transfer limiting conditions, such cellular characteristics are typically found to be of little significance at the biological steady state.³³ Thus, when effective microorganisms are used under a fixed set of operating condition, C_A is found to be influenced by the Henry's law constant because of its strong influence on the benzene transfer rate. Accordingly, because H_A is found to substantially control the absorption efficiency, so too does it have a remarkable influence on the efficiency of benzene removal in the TPPB. When originally deriving Eq. 20, rapid transfer and equilibrium were assumed. However, to better estimate the effect of organic solvent on the TPPB, TBTR into the TPPB was recalculated using experimental data in place of approximate relationships. For 9.1 mg/L of inlet benzene being fed to a single aqueous phase, and 9.5 mg/L of inlet benzene being supplied to a single organic phase, both at the same gas flow rate of 120 L/h, $k_{L,a_{\text{gas-A}}}$ and $k_{L,a_{\text{gas-O}}}$ were previously measured as 12.4 and 0.083 h⁻¹, respectively.³² In that study, the Henry's law constant for aqueous and organic phases were also given as 0.327 and 0.002, respectively, which yields a partitioning coefficient of 163.5 (Eq. 18). Although the inlet benzene concentrations differed by 0.4 mg/L, we selected a constant value of 9.5 mg/L for further calculations. The benzene transfer rates into the aqueous and organic phases, BTR_A and BTR_O, respectively, can be calculated as

$$\text{BTR}_A = 12.4(3.06 \times 9.5 - C_A)V_A \quad (22)$$

$$\begin{aligned} \text{BTR}_O &= 0.083 \times 163.5(3.06 \times 9.5 - C_A)V_O \\ &= 13.6(3.06 \times 9.5 - C_A)V_O \quad (23) \end{aligned}$$

where we can then calculate TBTR as

$$\text{TBTR} = \text{BTR}_A + \text{BTR}_O \quad (24)$$

These relationships are modeled in Figure 3, which clearly shows that POP has a very minor influence on TBTR and

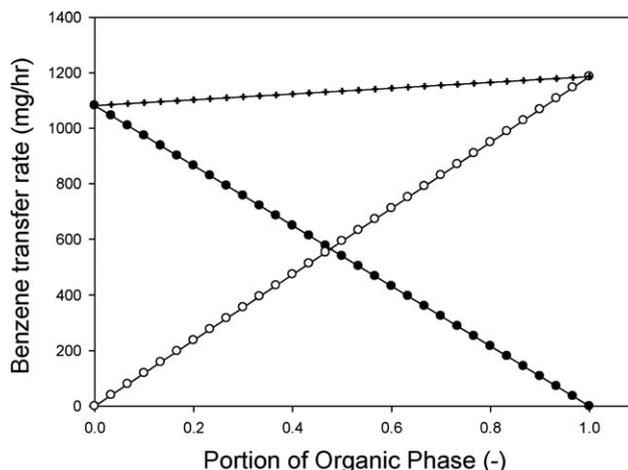


Figure 3. Benzene transfer rate into the aqueous and organic phases in the TPPB with 3 L of working volume.

●, benzene transfer rate into aqueous phase; ○, benzene transfer rate into organic phase; +, total benzene transfer rate into the TPPB.

the difference of TBTR between the two extreme cases of 0.0 and 1.0 POP is less than 10%. Examining Eqs. 22 and 23 more closely, we find that the benzene transfer rate coefficient into the aqueous phase, 12.4 h⁻¹, was very close to the product of that into the organic phase and the partitioning coefficient of benzene between two phases, 13.6 h⁻¹ (a difference of only 9.7%). In this study, an enhancement factor, indicating the increase of mass-transfer rate by adding organic solvent, is now defined by the product: $(P_{O-A} \times k_{L,a_{\text{gas-O}}}/k_{L,a_{\text{gas-A}}})$. The enhancement factor should be over 1.0 to ensure the beneficial effect of organic solvent on benzene mass transfer. Because the presence of cells and medium components could decrease solubility or increase H_A due to a salting-out effect^{34,35} more accurate estimates of H_A are required for the calculation of a more accurate enhancement factor.

When comparing the results of Figures 1 and 3, it seems that only TOTR should be considered in the process of POP determination because TOTR is substantially influenced by the solvent whereas TBTR remains largely insensitive. However, we must also consider the physical properties of benzene before validating this conclusion. Although benzene is volatile, it has relatively a high solubility in water (1,780 mg/L at 20°C).³⁶ To treat a much less polar VOC (with higher Henry's law constant or lower solubility in water), some of the VOC could escape from a reactor composed of only an aqueous phase without being absorbed. That is, when compared with benzene, a higher proportion of the inlet VOC could escape the reactor under similar operating conditions. If we then were to add an organic solvent toward which the VOC having a very low Henry's law constant, the VOC could be easily transferred to the organic solvent and a very low portion of the VOC would then escape from the TPPB. As previously stated, the effect of organic solvent addition is determined by an enhancement factor which would have a larger value for a nonpolar VOC because of the higher partition coefficient of the VOC between the organic solvent and water. If the enhancement factor is quite large, the organic solvent would play an important role in the mass transfer of a VOC into the TPPB.

As mentioned above, the low enhancement of the TBTR into the TPPB by the addition of *n*-hexadecane is mainly due to the low Henry's law constant (7.20×10^{-3} atm m³/mol).³⁷

This implies that an organic solvent would be more beneficial for the treatment of a compound with a low solubility in water. A similar report noted that mass-transfer rate enhancement by the addition of a second liquid phase is less significant for moderately poorly water-soluble compounds such as toluene compared with very poorly water-soluble ones such as oxygen.³⁸ Because the solubility of benzene in water is three times that of toluene (515 mg/L at 20°C),³⁶ the effect of organic solvent addition on the TBTR turned out to be much less significant than that on TOTR into the TPPB. Some other research treating *n*-hexane or α -pinene, poorly soluble contaminants, also showed that the performances of TPPB with organic solvent was enhanced by 5 and 12 times compared with the system without an organic phase.^{39–41}

Therefore, if we were to treat, for example, xylene isomers (H_A : 7.20×10^{-3} atm m³/mol, solubility: 172 mg/L), ethylbenzene (1.05×10^{-2} atm m³/mol, 152 mg/L), isopropylbenzene (1.37×10^{-2} atm m³/mol, 74 mg/L), cyclohexane (2.23×10^{-1} atm m³/mol, 55 mg/L), pentachlorophenol (20 mg/L), methylcyclohexane (14 mg/L), 1,2,4-trimethyl benzene (practically insoluble in water), or *n*-hexane (1.56 atm m³/mol, insoluble), the addition of a chosen organic solvent could increase the total transfer rates of these compounds into the TPPB, and thus enhance removal efficiencies.

Guideline for TPPB development

To generate a guide for others considering the application of TPPB technology for the treatment of VOCs, we have investigated various biological and engineering aspects associated with TPPBs such as cell mass requirement, and oxygen and VOC transfer rates with respect to various operating conditions. By reconfiguring the sequence of our above analysis, we can now provide a step-by-step procedure and general approach for the design and operation of TPPBs. Before starting, it should be noted that for the TPPB processes we have developed (and discussed here) the two liquid phases are completely mixed, behaving approximately as a homogeneous phase. Because the interfacial area and mass-transfer driving force between the two phases are sufficiently large, the assumptions of instantaneous equilibria of both pollutants and oxygen between the two phases were found to be valid. Thus, much of the analysis provided here remains reliant upon simplifying assumptions that are associated with such a condition. A diagram of the proposed strategy to be followed for the development of a TPPB for VOC treatment is shown in Figure 4.

TPPB development begins by defining the system of interest in terms of the target pollutants and appropriate degrading microorganism(s). It was assumed that the microorganisms used in the TPPB, either pure or mixed culture, were to have sufficient biocatalytic activity such that the system was not biodegradation rate limited. That is, the microorganisms should degrade the pollutants with acceptable high-degradation rate and have lower half-saturation constant and high-inhibition constant in the kinetic model of Andrews,⁴² for example. In addition, good design practices suggest that the selected microorganisms should not be pathogenic. For each target VOC of interest, H_A values should first be determined. H_A values for most VOCs of environmental interest are available in the literature, or may be readily determined experimentally. If it is desired to treat a VOC with low H_A , or relatively high solubility in water, one must further consider the magnitude of the inlet loading rate

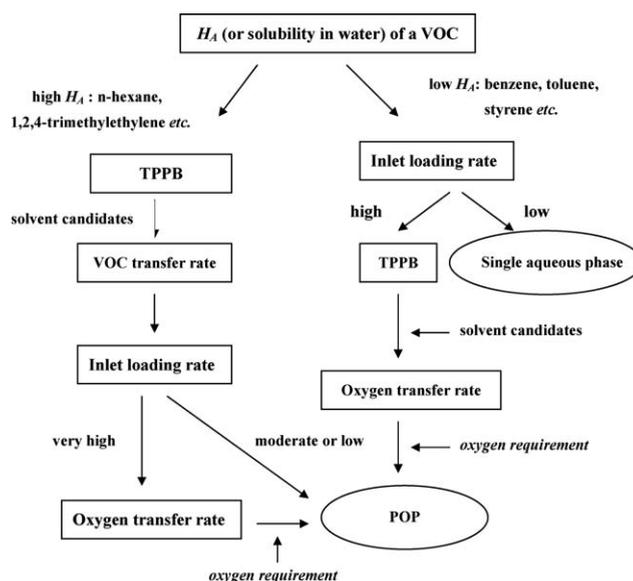


Figure 4. General strategy for the design of TPPBs.

which in turn determines the total oxygen requirement of the cells. If the inlet loading rate is low, a bioreactor with a single aqueous phase may provide adequate treatment of the VOC. In contrast, high-inlet loading rates may result in oxygen deficiencies, wherein an organic solvent can be added to increase the TOTR. In this case, we do not need to consider the VOC transfer rate enhancements resulting from the organic solvent, as the total transfer rate of the VOC will remain largely unchanged. For the selection of an ideal solvent, a rational selection procedure for solvent which will serve as the organic phase in the TPPBs was described in previous studies.^{30,41,43} That is, selection requires consideration of biological factors (biocompatibility and nonbioavailability), physical factors (volatility, density, hydrophobicity, and possibility of emulsification), chemical factors (handling and safety issues), and cost. In our study, we recommended a list of 2–3 candidate solvents for further consideration. The OTR into a single aqueous and an organic phase should then be measured through separate experiments and the POP can be determined as in section Determining the portion of organic phase.

On the other hand, to treat a VOC with high H_A , or low water solubility, a TPPB should then be selected for its enhanced mass-transfer characteristics. Solvent candidates should again be determined as described above, as high-removal efficiency cannot be achieved without high-mass-transfer rate of the VOC into the TPPB, which now becomes solvent-dependent. Therefore, to choose the best solvent, mass-transfer rates of the VOC into a single aqueous and an organic phase should first be experimentally characterized. Thereafter, if the inlet loading rate is expected to be high, OTRs should also be measured separately in single aqueous and organic phase experiments to determine the enhancement effect of organic solvent on the TOTR. The total oxygen requirement of the cells at biological steady state is then determined by the inlet loading rate, as described above, and POP can be determined as in section Determining the portion of organic phase. It should again be noted that every attempt to minimize POP should be taken to minimize capital and operating costs, provided that the VOC and oxygen transfer requirements of the TPPB remain uncompromised.

Conclusions

To prescribe a strategic approach for the design and operation of TPPBs, we have reviewed several earlier publications, reanalyzed several sets of data, and drawn valuable insights which have arisen from continued efforts in TPPB design and operation in our Group, and by others. Using a previously determined maintenance coefficient, we further determined the cell mass requirements at biological steady state for different VOC loading rates. The demand of oxygen by cells at biological steady state was calculated using available experimental data and the TOTR into the TPPB was calculated at different agitation and aeration rates. The results clearly indicate that gas flow rate or aeration rate significantly influence the TOTR into the TPPB, whereas agitation has a minor affect. By measuring the TOTR into the TPPB (as maintaining 50% of DO saturation) with an agitation rate of 400 rpm, it was predicted that oxygen limitations would not arise for BLRs as high as 822.5 mg/h, or an inlet benzene concentration of 13.7 mg/L flowing at 60 L/h. Through parametric sensitivity analysis at the biological steady state, it was found that the POP, partitioning of oxygen between two phases, and aeration rate all show similar effects on the TOTR into the TPPB. However, because of the ease with which it may be manipulated, we suggest POP to be the primary parameter to alter the total TPPB OTR, as required. However, as only the aqueous phase contains cells, one should deliberately consider the increase of cell density in the aqueous phase with increasing POP, which means there should be a limit to POP. Although the presence of an organic solvent in the TPPB remarkably increased the TOTR, the total benzene transfer rate into the TPPB remained largely insensitive due to the intrinsic low Henry's law constant of benzene in water. Finally, we have presented a step-by-step guideline by which other researchers may design TPPB systems for the control and treatment of VOCs for their own applications of interest.

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