

A Two-Phase Partitioning Airlift Bioreactor for the Treatment of BTEX Contaminated Gases

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Received 29 January 2008; revision received 24 March 2009; accepted 26 March 2009

Published online 3 April 2009 in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/bit.22343

ABSTRACT: This investigation characterizes a novel 11 L airlift two-phase partitioning bioreactor (TPPB) for the treatment of gases contaminated with a mixture of benzene, toluene, ethylbenzene, and *o*-xylene (BTEX). The application of the TPPB technology in an airlift bioreactor configuration provides a novel technology that reduces energy intensity relative to traditional stirred tank TPPB configurations. The addition of a solid second phase of silicone rubber beads (10%, v/v) or of a liquid second phase of silicone oil (10%, v/v) resulted in enhanced performance of the airlift bioreactor relative to the single phase case, with 20% more BTEX being removed from the gas phase during an imposed transient loading. During a 4 h loading step change of three times the nominal loading ($60 \text{ g m}^{-3} \text{ h}^{-1}$), overall removal efficiencies for the airlift TPPBs containing a liquid or solid phase remained above 75%, whereas the single phase airlift had an overall removal efficiency of 47.1%. The airlift TPPB containing a silicone rubber second phase was further characterized by testing performance during steady-state operation over a range of loadings and inlet gas flow rates in the form of a 3^2 factorial experimental design. Optimal operating conditions that avoid oxygen limitations and that still have a slow enough gas flow rate for sufficient BTEX transfer from the gas phase to the working volume are identified. The novel solid-liquid airlift TPPB reduces energy inputs relative to stirred tank designs while being able to eliminate large amounts of BTEX during both steady-state and fluctuating loading conditions. *Biotechnol. Bioeng.* 2009;103: 1077–1086.

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KEYWORDS: airlift; biodegradation; BTEX; microbial consortium; partitioning bioreactor

Introduction

Printing facilities (Thanacharoenchanaphas et al., 2007), petroleum refineries (Stewart et al., 2001) and contaminated sites undergoing remediation (Liang et al., 2009) are all

sources of gaseous emissions of benzene, toluene, ethylbenzene, and *o*-xylene (BTEX). Due to the toxicity of BTEX components, treatment of these waste gas streams is needed in order to meet regulatory emission standards. Biological treatment methods, such as biofilters, can provide a low-cost, energy efficient, and effective solution for the degradation of BTEX. However, biofilters can have limitations such as bed drying, biomass clogging, and the inability to effectively handle fluctuations in loading (Khan and Ghoshal, 2000). Therefore, there has been recent interest in the design and improvement of novel biological BTEX treatment systems that have the ability to operate beyond the current abilities of biofilters (Kan and Deshusses, 2005; Studer and von Rohr, 2008). However, design of novel biological treatment systems can often involve stirred tank reactors, which are energy intensive and compromise the energy benefits that are typically associated with biological treatment methods. A solution to this is the implementation of airlift bioreactors, which can provide a low energy alternative to traditional stirred tanks.

An example of such a novel biological treatment method that has been researched to date primarily in stirred tank vessels is the two-phase partitioning bioreactor (TPPB), which is gaining popularity for the destruction of toxic compounds in waste gases (Aldric and Thonart, 2008; Arriaga et al., 2006; Bailon et al. 2009; Muñoz et al., 2008). TPPBs consist of a cell containing aqueous phase and a non-toxic, non-bioavailable second phase that can sequester high and fluctuating concentrations of toxic substrates and release them to the aqueous phase for subsequent degradation based on microbial metabolic demand. This provides the ability to treat fluctuating concentrations of toxic compounds with low water solubility by alleviating toxic levels in the aqueous phase and improving mass transfer out of the gas phase. Silicone oil has been traditionally used as the immiscible phase in a TPPB and is non-bioavailable to microbial consortia, however, because of its fixed chemical structure, silicone oil cannot be modified for optimal uptake and release of target molecules.

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Although other organic solvents can be selected for treatment of a particular contaminant based on pairing with the target molecule, they are typically limited to systems that treat single VOCs and the use of pure strains of microorganisms due to the potential bioavailability of the organic solvent. This limits the use of other organic solvent second phases for BTEX mixtures, as treatment of waste gases containing BTEX requires the use of a bacterial consortium, since there is no known pure strain of bacteria with the ability to effectively degrade all BTEX components (Bielefeldt and Stensel, 1999). An alternative to a second liquid phase in a TPPB is solid polymers, as they can be selected based on pairing the polymer with the contaminant molecule and they are typically non-bioavailable to bacteria. Littlejohns and Daugulis (2008a) have recently utilized solid silicone rubber polymer beads as the second phase in a 3 L stirred tank TPPB containing a microbial consortium to treat transient loadings of BTEX.

The objective of most research to date on suspended cell TPPBs has been directed towards characterizing the abilities and performance of these systems for different applications and under a variety of operating conditions (Malinowski, 2001) and, therefore, as mentioned previously, traditional stirred tanks have been used. Although stirred tanks provide a convenient configuration for preliminary investigation, scale-up of mechanically agitated TPPBs is constrained by their energy intensity. Airlift bioreactors require less energy, and therefore, facilitate design scale-up, providing a potential practical replacement for traditional mechanically agitated configurations. This research is the first investigation of a TPPB in an airlift configuration with the objective of providing an enhanced biotreatment option with reasonable energy inputs for industrial use.

There were three main objectives in the investigation of this novel TPPB system: (1) To perform an initial scoping investigation of the airlift TPPB by operating with a second phase of silicone rubber beads (solid–liquid airlift TPPB) and a single phase airlift (control airlift) for the treatment of a continuous gas stream contaminated with BTEX. This initial scoping consisted of operation of both systems until steady-state biomass concentration was reached at a nominal loading of $20 \text{ g m}^{-3} \text{ h}^{-1}$, followed by a 4 h BTEX step change of two times that nominal loading ($2\times$). The performance of the solid–liquid airlift TPPB was also compared to the performance of the solid–liquid mechanically agitated TPPB investigated by Littlejohns and Daugulis (2008a). (2) To subject both airlift systems described in the scoping study to an increased step change loading of three times the nominal loading ($3\times$) in order to approach limits of system operation. In addition, an airlift containing a second phase of silicone oil (liquid–liquid airlift TPPB) was tested at these conditions in order to provide the solid–liquid airlift TPPB a comparison to a more conventional second phase found in TPPB literature. (3) To identify optimal steady-state operating regions for the solid–liquid airlift TPPB over a range of gas flow rates and BTEX loadings.

Materials and Methods

Chemicals

Benzene and *o*-xylene were obtained from Sigma–Aldrich (Oakville, Canada), and toluene and ethylbenzene were obtained from Fisher Scientific (Nepean, Canada). All chemicals used for the fermentation medium were obtained from either Sigma–Aldrich or Fisher Scientific.

Selection of Partitioning Phases

Silicone rubber, primarily composed of polydimethylsiloxane, was obtained from GE (Huntersville, NC) in the form of 100% silicone rubber caulking. The caulking was dried to approximately spherical shaped beads of density 1.15 g L^{-1} and diameter 2.2 mm. The rationale for selecting silicone rubber as the partitioning phase was based on consideration of BTEX partitioning between the liquid and polymer phases, diffusivity through the polymer, and polymer bioavailability, as described in Littlejohns and Daugulis (2008a). An additional polymer selection criterion for an airlift TPPB is that the polymer must be suspended throughout the airlift bioreactor by liquid velocities induced by gas flow rates within the typical airlift operating range, due to the airlift bioreactor not being mechanically agitated. A range of polymers (those tested in Littlejohns and Daugulis, 2008a) were examined for suspension under a range of flow rates from 1 to 5 L min^{-1} and it was determined that silicone rubber was the easiest to suspend due to its density ($1,150 \text{ g L}^{-1}$) being only slightly higher than that of water.

Silicone oil with viscosity 5 cSt, obtained from Sigma–Aldrich, was the liquid partitioning phase that was selected for comparison, as it is non-bioavailable to microorganisms and can therefore be used with the BTEX degrading bacterial consortium. In addition, it is used as the sequestering phase in TPPBs by a number of other authors (Aldric and Thonart, 2008; Gardin et al., 1999; Muñoz et al., 2007).

Microorganisms

The bacterial consortium used in all experimentation was enriched from petroleum-contaminated soil as previously described (Littlejohns and Daugulis, 2008b). A denaturing gradient gel electrophoresis was performed by Microbial Insights (Rockford, TN), which revealed that the consortium used in all experimentation in the current study consists of seven different species of *Pseudomonas*.

Experimental Setup

The experimental setup for the solid–liquid airlift TPPB is shown in Figure 1. The bioreactor used was a 13 L Chemap AG Series 3000 Fermentor (Männedorf, Switzerland) with

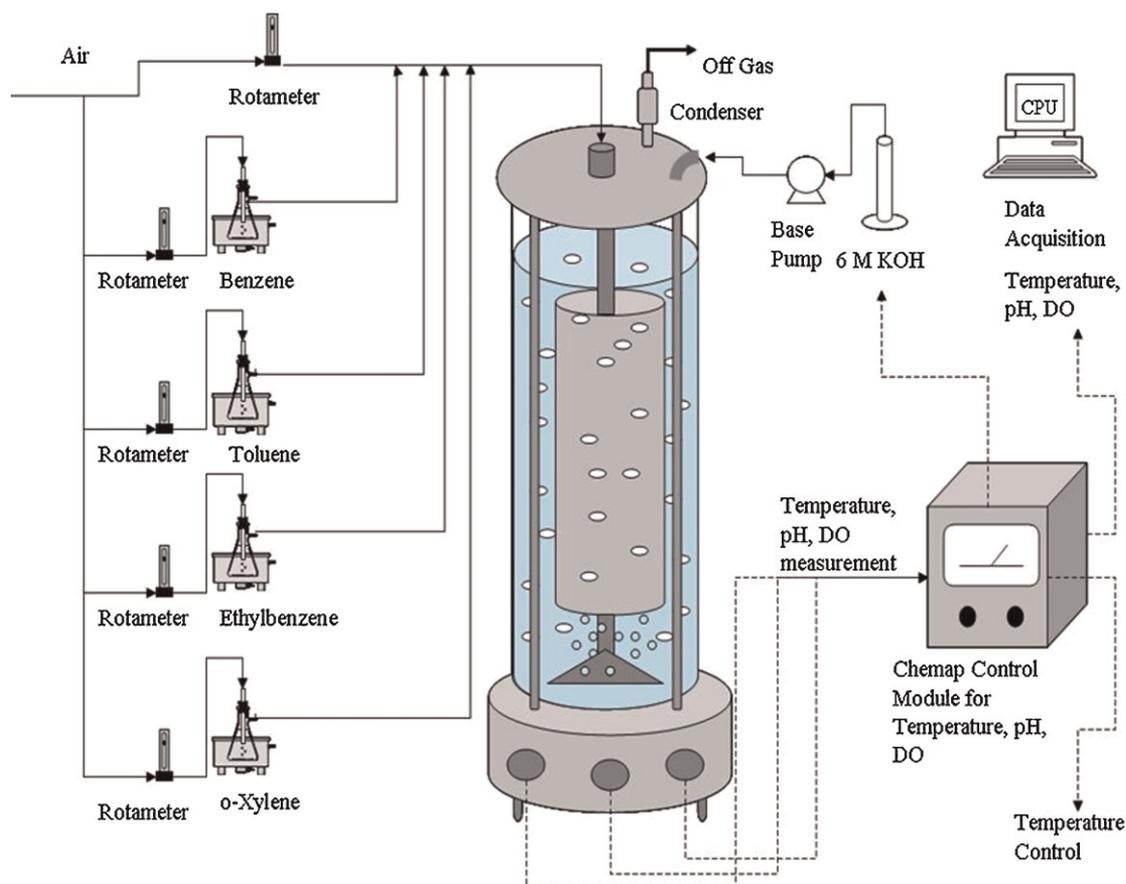


Figure 1. Experimental setup for a solid-liquid airlift TPPB for the treatment of BTEX. [Color figure can be seen in the online version of this article, available at www.interscience.wiley.com.]

dimensions listed in Table I. The airlift had a total working volume of 11 L with either 10% silicone rubber polymer beads, 10% silicone oil, or without a second phase. The aqueous phase had the following composition (g L^{-1}); 7 $(\text{NH}_4)_2\text{SO}_4$, 0.75 $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 6.6 K_2HPO_4 , 8.42 KH_2PO_4 , and 1 mL L^{-1} trace elements. The trace element solution consisted of (g L^{-1}); 16.2 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 9.44 CaHPO_4 , 0.15 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and 40 citric acid. Each bioreactor run was inoculated at an initial biomass concentration of 0.5 g L^{-1} . Throughout experimental runs, the temperature was maintained at 30°C and the pH was maintained at 6.9 by the addition of 6 M KOH. The dissolved oxygen (DO) concentration was monitored continuously during all experimentation using an Ingold (Mississauga, Canada) polarographic probe.

Experimental Conditions

Before step change operation, each airlift bioreactor system was operated under nominal conditions until steady-state biomass concentrations were achieved ($>150 \text{ h}$). Biomass concentrations reached a steady-state, even with the continued addition and consumption of substrate, due to the substrate being directed towards maintenance purposes rather than cell growth (Nielsen et al., 2005a). Under nominal conditions before and after step changes, the gas stream had a flow rate of 3 L min^{-1} (empty bed residence time (EBRT) of 3.7 min^{-1}) and a BTEX concentration, which corresponds to a loading of $20 \text{ g m}^{-3} \text{ h}^{-1}$. The inlet gas phase for all experimentation contained approximately equal proportions of benzene, toluene, ethylbenzene, and

Table I. Geometry of airlift bioreactor.

D_T (m) tank diameter	D_R (m) riser diameter	h_T (m) tank height	h_R (m) riser height	A_d/A_r downcomer cross-sectional area/ riser cross-sectional area	V_r (L) riser volume	V_d (L) downcomer volume	V_T (L) total volume
0.14	0.1	0.76	0.53	1.96	4.16	4.43	11

o-xylene. During step changes of 2× and 3× (40 and 60 g m⁻³ h⁻¹, respectively), the concentration in the inlet gas was increased and the gas flow rate remained constant.

During steady-state investigation of the solid–liquid airlift TPPB, nine conditions were tested in a 3² factorial experimental design for gas flow rates of 2, 3, and 4 L min⁻¹ (EBRT of 5.5, 3.7, and 2.75 min⁻¹, respectively) and BTEX loadings of 20, 60, and 100 g m⁻³ h⁻¹.

Sampling Procedure

Samples of the gaseous stream at the entry and exit of the bioreactor were taken approximately every 12 h during operation leading to steady-state and during steady-state operation, and every 13 min during imposed BTEX step changes. Gas phase samples were analyzed by GC/FID using a method described elsewhere (Littlejohns and Daugulis, 2008b). Aqueous phase samples from the bioreactor were also taken at the time of gas sampling in order to monitor biomass concentrations, which were determined by optical density measurements at 600 nm with a Biochrom Ultraspec 3000 UV/vis spectrophotometer (Cambridge, UK) and compared to a calibration curve relating optical density to cell dry weight.

Samples of the aqueous and polymer phases in the solid–liquid airlift TPPB during step change transients were taken approximately every 40 min and concentrations in both phases were determined as described previously (Littlejohns and Daugulis, 2008a) using partition coefficients for BTEX in polymer which were previously determined to be 62 ± 2, 200 ± 4, 593 ± 5, and 414 ± 2 mg L⁻¹ polymer phase L mg⁻¹ liquid phase for benzene, toluene, ethylbenzene, and *o*-xylene, respectively. Concentrations in the aqueous phase for the control airlift were determined by taking a 10 mL sample of the reactor and quickly injecting it into an airtight 125 mL glass bottle containing 10 drops of pure phosphoric acid to immediately kill bacteria in the sample. The bottles were left to equilibrate over 12 h and then headspace concentrations were determined using GC/FID. Using Henry's constants of 0.26, 0.35, 0.43, and 0.25 mg L⁻¹ gas phase mg⁻¹ L aqueous phase for benzene, toluene, ethylbenzene, and *o*-xylene, respectively (Littlejohns and Daugulis, 2008a), concentrations in the original aqueous phase sample were then estimated. Concentrations in the aqueous and silicone oil phases in the liquid–liquid airlift TPPB were determined by taking a 10 mL sample of the mixed reactor contents and quickly injecting it into an airtight 125 mL glass bottle containing 10 drops of pure phosphoric acid. Again, the bottles were left to equilibrate over 12 h and then headspace concentrations were determined. By assuming that the silicone oil and aqueous phase were in equilibrium in the bioreactor, and by using Henry's constants and partition coefficients for BTEX components between aqueous and oil phases, the concentrations in the aqueous and oil phases in the original sample were determined. Partition coefficients between aqueous and

silicone oil phases were previously determined by adding a known amount of each BTEX component into an airtight bottle containing 10 mL silicone oil, 40 mL aqueous phase, and 75 mL headspace. By measuring headspace concentrations and using Henry's constants, partition coefficients for benzene, toluene, ethylbenzene, and *o*-xylene were determined to be 103, 312, 909, and 666 mg L⁻¹ oil phase mg⁻¹ L aqueous phase.

Performance Indicators

Instantaneous performance indicators for VOC gas treatment systems include removal efficiency (RE) and elimination capacity (EC) which are shown as Equations (1) and (2), respectively

$$RE = \frac{S_g^{\text{in}} - S_g^{\text{out}}}{S_g^{\text{in}}} \times 100\% \quad (1)$$

$$EC = \frac{Q_g(S_g^{\text{in}} - S_g^{\text{out}})}{V_{\text{total}}} \quad (2)$$

where Q_g is the gas flow rate (L h⁻¹), S_g^{in} the instantaneous concentration of BTEX in the inlet gas (g L⁻¹), S_g^{out} the instantaneous concentration of BTEX in the outlet gas (g L⁻¹), and V_{total} the working volume of the TPPB (m⁻³).

During transient periods, overall RE and EC, or cumulative RE and EC, are also useful performance indicators that account for stripping from the working volume after the completion of a step change. The period during which these performance indicators are determined is from the initiation of the transient period until performance has stabilized to nominal output conditions after the step change completion. Overall RE and EC are shown as Equations (3) and (4), respectively

$$RE_{\text{overall}} = \frac{\sum_{i=1}^n (S_{g,i}^{\text{in}} - S_{g,i}^{\text{out}})}{\sum_{i=1}^n (S_{g,i}^{\text{in}})} \times 100\% \quad (3)$$

$$EC_{\text{overall}} = \frac{Q_g}{V_{\text{total}} t_{\text{overall}}} \sum_{i=1}^n (S_{g,i}^{\text{in}} - S_{g,i}^{\text{out}}) t_{i,i+1} \quad (4)$$

where i is the sample number, n is the total number of samples taking during the overall period of transient performance due to the step change, t_{overall} is the time of the overall transient performance due to the step change (min) and $t_{i,i+1}$ is the time between sample i and the next proceeding sample (min).

Results and Discussion

Initial Scoping Investigation

The initial experiments, which consisted of BTEX step changes of $2\times$, were performed in order to obtain an indication of how well the solid–liquid airlift TPPB would perform relative to both a control airlift as well as a solid–liquid stirred tank TPPB with identical composition previously reported by Littlejohns and Daugulis (2008a). Both airlift bioreactor systems were operated at the nominal loading of $20\text{ g m}^{-3}\text{ h}^{-1}$ for at least 150 h until steady-state biomass concentrations were reached, at which time the 4 h transients of $2\times$ were introduced (Fig. 2a). At the nominal loadings, prior to step changes, performances of both systems were similar, as average REs of 75.8% and ECs of $18.7\text{ g m}^{-3}\text{ h}^{-1}$ were achieved for the solid–liquid airlift TPPB and average REs of 72.3% and ECs of $17.9\text{ g m}^{-3}\text{ h}^{-1}$ were achieved for the control airlift. In general, during both nominal loadings, as well as step changes, there was a trend of removal being highest for toluene > benzene > ethylbenzene > *o*-xylene.

During the BTEX step changes (Fig. 2a), the overall RE and EC were 73.8% and $27.3\text{ g m}^{-3}\text{ h}^{-1}$, respectively, for the system with polymers and 53.2% and $21.5\text{ g m}^{-3}\text{ h}^{-1}$ respectively, for the system without polymers. During the $2\times$ step change, biodegradation of specific compounds was

of the order toluene (60.8%), ethylbenzene (57.9%), benzene (55.2%), and *o*-xylene (46.1%), for the airlift without polymers, and toluene (82.6%), ethylbenzene (74.8%), benzene (71.2%), and *o*-xylene (63.5%), for the airlift-containing polymers. Therefore, the benefits of a sequestering phase become most obvious during transient periods, which is a result that has also been observed for stirred tank TPPBs (Daugulis and Boudreau, 2008). It should be noted that, due to fluctuations in rotameter settings during step changes, there are instances where both systems have similar ECs with different REs, which can be seen, for example, at $t=100, 155,$ and 210 in Figure 2a. Comparison between the solid–liquid stirred tank TPPB at a nominal loading of $60\text{ g m}^{-3}\text{ h}^{-1}$ (Littlejohns and Daugulis, 2008a) and the solid–liquid airlift TPPB at a nominal loading of $20\text{ g m}^{-3}\text{ h}^{-1}$ reveals that the latter removes 20% less from the gas stream during steady-state and transient periods. This suggests that BTEX mass transfer limitations may be a concern for the airlift. However, the airlift system still has the ability to reduce off gas concentrations significantly. In addition, the initial scoping experiments demonstrated the ability of the solid–liquid airlift TPPB to buffer fluctuations in inlet loading relative to a single phase airlift, which is a very useful characteristic in industrial settings, as feed fluctuations commonly occur (Stewart et al., 2001).

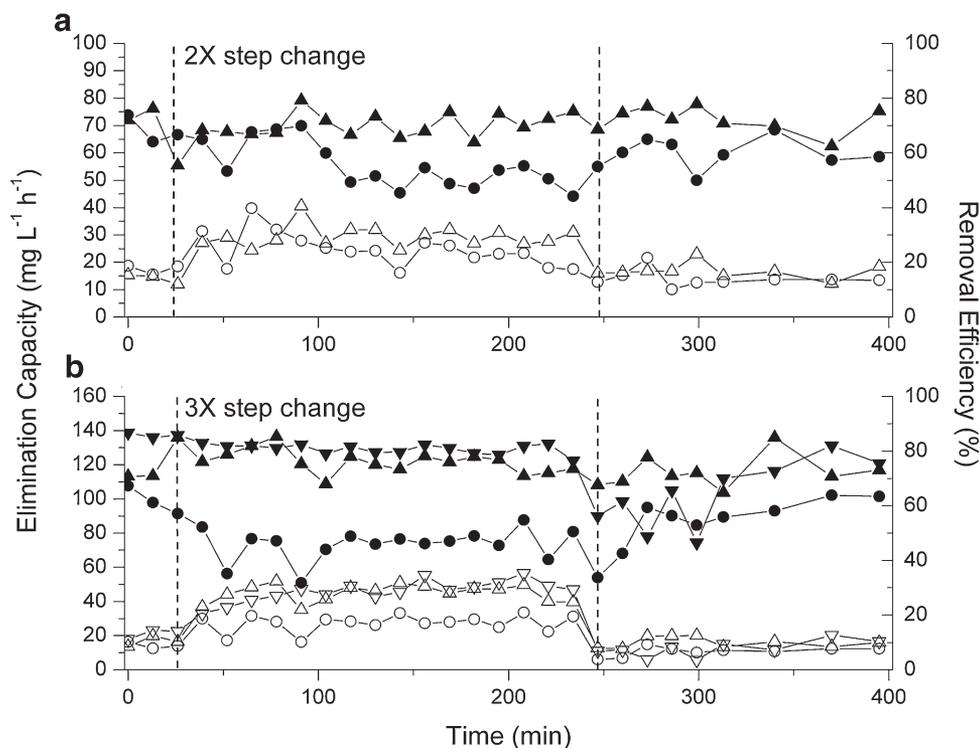


Figure 2. a: Step change of $2\times$ for solid–liquid airlift TPPB (triangles) and control airlift (circles), RE—solid shapes, EC—hollow shapes. b: Step change of $3\times$ for solid–liquid airlift TPPB (triangles), liquid–liquid airlift TPPB (inverted triangles), and control airlift (circles), RE—solid shapes, EC—hollow shapes. Dotted lines represent the start and end of the step change.

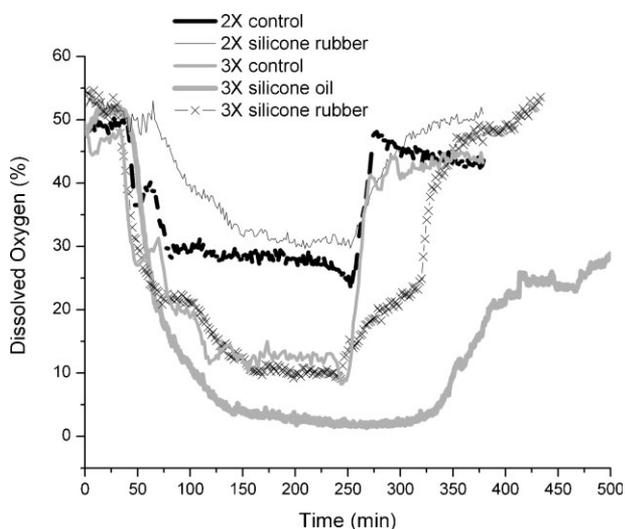


Figure 3. Dissolved oxygen traces for step changes of 2× for solid–liquid airlift TPPB and control airlift and 3× for solid–liquid airlift TPPB, liquid–liquid airlift TPPB, and control airlift.

The DO traces for both airlift systems for the 2× transient are shown in Figure 3. It can be seen that the DO decreased for both systems upon the initiation of the increased BTEX loading followed by an increase back to nominal levels after

the completion of the step change. However, it took the solid–liquid airlift TPPB longer to reach original DO levels compared to the control airlift after the completion of the transient. This has been observed in previous TPPB literature (Boudreau and Daugulis, 2006) and has been attributed to the additional oxygen requirements needed to degrade the substrate sequestered by the polymer during the transient that is partitioned back to the aqueous phase upon completion of the step change.

In order to confirm that the polymer beads were sequestering BTEX from the aqueous phase during the step change and releasing the BTEX after the loading was returned to nominal levels, BTEX concentrations in the aqueous and silicone rubber phases were determined and are shown in Figure 4a. As can be seen, aqueous phase BTEX concentrations are much lower in the solid–liquid airlift TPPB compared to the control airlift (0.06 mg L^{-1} vs. 2.25 mg L^{-1}), suggesting that the polymer beads buffer the aqueous BTEX concentrations during inlet fluctuations. This may account for the superior performance of BTEX removal by the airlift-containing polymers, as the driving force for BTEX transfer from the gas phase into the liquid phase is increased. It can also be seen that much higher concentrations of BTEX are present in the polymer beads relative to the aqueous phase in the solid–liquid airlift TPPB (approximately 400 times), again indicating that the second phase serves to buffer aqueous phase concentrations.

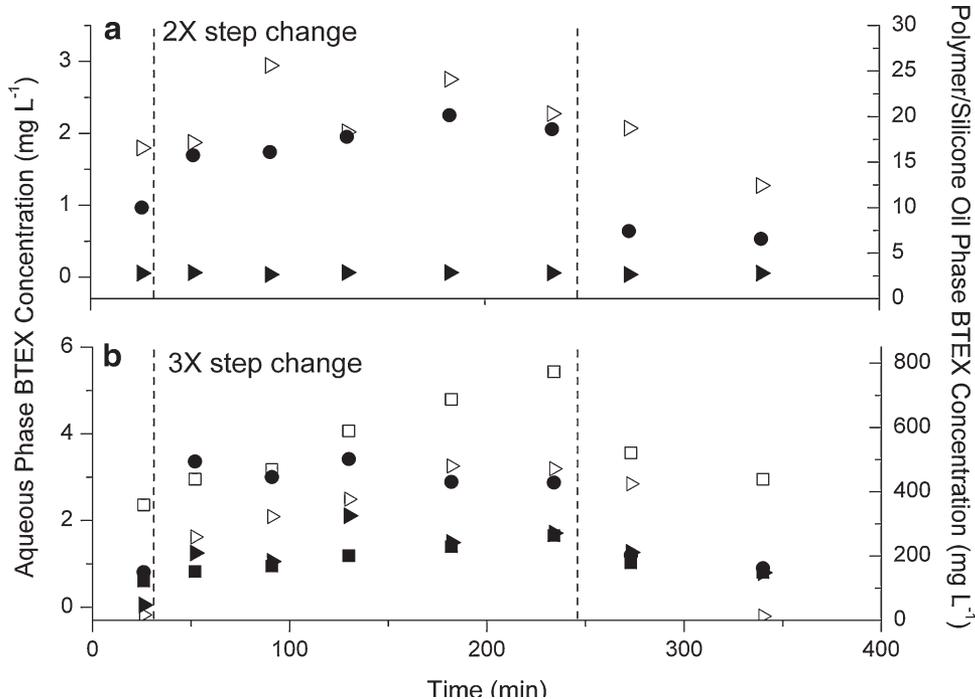


Figure 4. a: During a step change of 2×; concentrations in a solid–liquid airlift TPPB in the aqueous phase (solid triangle) and polymer phase (hollow triangle) and concentrations in the control airlift aqueous phase (solid circle). b: During a step change of 3×; concentrations in a solid–liquid airlift TPPB in the aqueous phase (solid triangle) and polymer phase (hollow triangle), concentrations in the liquid–liquid airlift TPPB in the aqueous phase (solid square) and silicone oil phase (hollow square), and concentrations in the control airlift aqueous phase (solid circle). Dotted lines represent the start and end of the step change.

At time = 234 min, the polymer beads contained 97% of the total BTEX present in the airlift TPPB. These results are comparable to those for a stirred tank TPPB wherein 93% of the total BTEX present in the bioreactor was in the polymer phase during a step change of 2× (Littlejohns and Daugulis, 2008a).

Increased Step Change Loading of 3×

To further explore the operation of the airlift system under transient loading, step changes of 3× were undertaken for the solid–liquid airlift TPPB, the control airlift, and also for the liquid–liquid airlift TPPB with a silicone oil sequestering phase. Silicone oil was tested to give a direct comparison between a second phase of polymer beads and traditional silicone oil in an airlift TPPB, as silicone oil is a common material used in liquid–liquid TPPBs (Aldric and Thonart, 2008; Gardin et al., 1999; Muñoz et al., 2008). Table II displays the performance of all three airlift systems during steady-state operation before the introduction of the step changes, and shows comparable performance by the three systems. This result is in agreement with Nielsen et al. (2007) who showed that the addition of an *n*-hexadecane phase into a bioreactor only slightly increases steady-state performance for the treatment of a benzene contaminated gas stream, while Bailon et al. (2009) have shown that the addition of a silicone oil phase significantly increased performance at steady-state for the treatment of a dichloromethane contaminated gas stream. The higher biomass concentration for the liquid–liquid airlift TPPB and the solid–liquid TPPB seen in Table II may be attributed to the buffering of substrates during the dynamic period of bioreactor start-up, allowing biomass to reach higher steady-state levels. The higher biomass concentrations in the silicone oil system relative to the polymer-containing system may be due to the uptake and release of substrates by silicone oil being instantaneous, whereas the uptake and release of silicone rubber is much slower.

Results of the step change of 3× nominal loading for all airlift systems are shown in Figure 2b, which further demonstrates the buffering abilities of the TPPB airlift systems during dynamic loadings. The RE for the control airlift dropped to an average of 45% during the transient, whereas the REs for both TPPBs remained above 75%. The performance for both the TPPB systems were quite similar during the transient period, as the overall RE and EC for the solid–liquid airlift TPPB was 75.4% and 38.6 g m⁻³ h⁻¹,

respectively, and the overall RE and EC for the liquid–liquid airlift TPPB was 75.0% and 37.2 g m⁻³ h⁻¹, respectively. The control airlift had much lower performance, with an overall RE and EC of 47.1% and 21.7 g m⁻³ h⁻¹, respectively. During the 3× step change, biodegradation of specific compounds was of the order toluene (58.9%), ethylbenzene (57.8%), benzene (48.3%), and *o*-xylene (25.5%), for the single phase airlift, toluene (81.2%), ethylbenzene (79.8%), benzene (71.4%), and *o*-xylene (65.6%), for the airlift-containing polymers, and toluene (87.2%), ethylbenzene, benzene (78.7%), ethylbenzene (71.1%), and *o*-xylene (65.9%), for the airlift-containing silicone oil. DO traces for all three systems for the 3× step change can be seen in Figure 3. Although DO levels decreased during the step change in all cases, the DO in the airlift TPPBs took much longer to recover with the liquid–liquid airlift TPPB taking the longest. Figure 3 shows that during the step change of 3×, oxygen-limiting conditions were likely being approached.

Concentrations in the aqueous, silicone rubber, and silicone oil phases were also determined during the 3× transients and are reported in Figure 4b. Aqueous phase BTEX concentrations are lower in the solid–liquid TPPB (<2.1 mg L⁻¹) and the liquid–liquid TPPB (<1.8 mg L⁻¹) in comparison to the control airlift (<3.5 mg L⁻¹), showing sequestration of BTEX from the liquid phase during inlet fluctuations. This sequestration is further demonstrated by the fact that at time = 234 min, the polymer beads contained 96% and the silicone oil contained 98% of the total BTEX present in the airlift bioreactors. These results are comparable to those for a stirred tank configuration wherein 91% of the total BTEX present in the bioreactor was in the polymer beads during a step change of 4× the nominal loading (Littlejohns and Daugulis, 2008a). This suggests that, the use of a second phase to sequester VOCs during fluctuating inlet loadings is beneficial to a biotreatment system, regardless of whether the bioreactor is in airlift or stirred tank configuration.

Although the current results show that the liquid–liquid airlift TPPB and the solid–liquid airlift TPPB have similar performance during fluctuating inlet loadings, there are numerous benefits to using a polymer phase in comparison to an immiscible liquid, including the fact that polymers are generally much less expensive, are non-volatile, can be formed into many shapes and sizes, and are generally non-hazardous environmentally and for operators. From transient loading investigations, however, it has become apparent that both oxygen and BTEX mass transfer

Table II. Performance for airlift systems at steady-state operation for a loading of approximately 20 mg L⁻¹ h⁻¹.

System	Duration of operation before reaching SS (h)	EC (mg L ⁻¹ h ⁻¹)	RE (%)	Biomass (g L ⁻¹)	DO (%)
Control (no second phase)	177	18.3 ± 4.3	72.3 ± 11.3	1.10	47
With polymers	165	18.5 ± 4.9	75.3 ± 8.1	1.42	53
With oil	189	19.0 ± 3.8	78.6 ± 5.2	2.09	50

limitations are concerns during airlift operation. Therefore, in order to further characterize the impact that potential mass transfer limitations may have on solid–liquid TPPB performance, the effect of loading and inlet gas flow rate during steady-state operation was determined.

Identification of Optimal Steady-State Operating Regions for Solid–Liquid TPPB

Inlet gas flow rates and loadings were varied in the form of a 3^2 factorial experimental design, and the solid–liquid airlift TPPB was operated under each set of conditions until steady-state biomass concentrations were reached (>150 h for each condition). The average RE and EC and the respective standard errors can be seen for each set of operating conditions in Figure 5. This plot shows a similar decrease in RE as loading is increased from 60 to 120 $\text{g m}^{-3} \text{h}^{-1}$ for all flow rates. However, at the lowest loading condition of 20 $\text{g m}^{-3} \text{h}^{-1}$, there are differences in performance for different inlet gas flow rates, with flow rate of 3 L min^{-1} achieving the maximum RE. This may be explained in part by consideration of Figure 6a. It can be seen that at a flow rate of 2 L min^{-1} , the system appears to be oxygen limited under all loadings tested. At flow rates of 3 and 4 L min^{-1} the system is not oxygen limited, however, at a flow rate of 4 L min^{-1} the EBRT is too small for effective BTEX mass transfer from the gas phase to the liquid phase. VOC mass transfer limitations during high inlet flow rates in airlift bioreactors that result in decreases in system performance have been observed by other authors including Vergara-Fernández et al. (2008) who used an internal loop airlift bioreactor to treat toluene, and Harding et al. (2003)

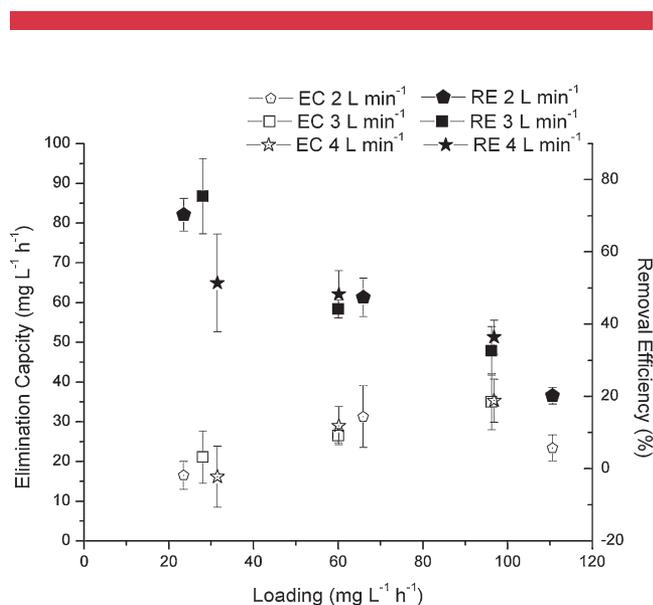


Figure 5. Steady-state ECs and REs for solid–liquid airlift TPPB under varying flow rates and loadings.

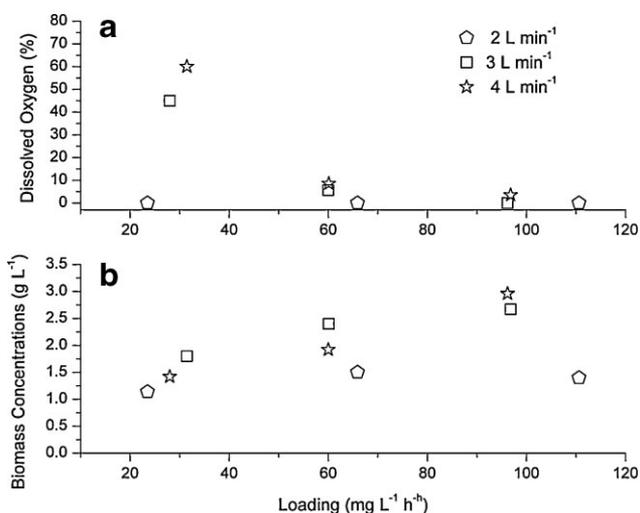


Figure 6. a: Steady-state DO concentrations for solid–liquid airlift TPPB under varying gas flow rates and loadings. b: Steady-state biomass concentrations for solid–liquid airlift TPPB under varying gas flow rates and loadings.

who used an external loop airlift bioreactor with a spinning sparger for the treatment of toluene. Therefore, there exist optimal operating regions for the airlift bioreactor that avoid oxygen limiting conditions while having a high enough EBRT for contaminants to transfer out of the gas phase. Figure 6a and b also demonstrate the impact that DO levels can have on steady-state biomass concentrations. Since airlift TPPB operation at a flow rate of 2 L min^{-1} is oxygen limited under all loadings (Fig. 6a), the biomass concentrations at 2 L min^{-1} remain constant despite an increase in loading (Fig. 6b). Operation at flow rates of 3 and 4 L min^{-1} has a DO of greater than 0% for all loadings, and it can be seen that biomass levels steadily increase as loading is increased. In comparison to the mechanically agitated solid–liquid TPPB investigated by Littlejohns and Daugulis (2008a), steady-state biomass concentrations are much lower in the current study likely due to the lower loadings and lower REs achieved. However, Figure 7 shows a linear correlation between the average EC of the airlift TPPB and steady-state biomass concentrations. Therefore, despite oxygen limitations, the BTEX removed from the gas corresponds to the biomass growth in the reactor.

In comparison to traditional biotreatment methods, the airlift TPPB provides comparable performance at steady-state. For example, Zilli et al. (2004) investigated the removal of benzene using traditional biofiltration and received maximum ECs of 3.2 , 6.4 , and 26 $\text{g m}^{-3} \text{h}^{-1}$ with REs of 52% , 53% , and 84% , for packing materials of raw sugarcane, sieved sugarcane, and peat, respectively. In addition, Kamarthi and Willingham (1994) determined ECs of 20 – 30 $\text{g m}^{-3} \text{h}^{-1}$ for REs of 70 – 90% for a biofilter containing compost media treating BTEX. As previously stated, there has been recent interest in developing

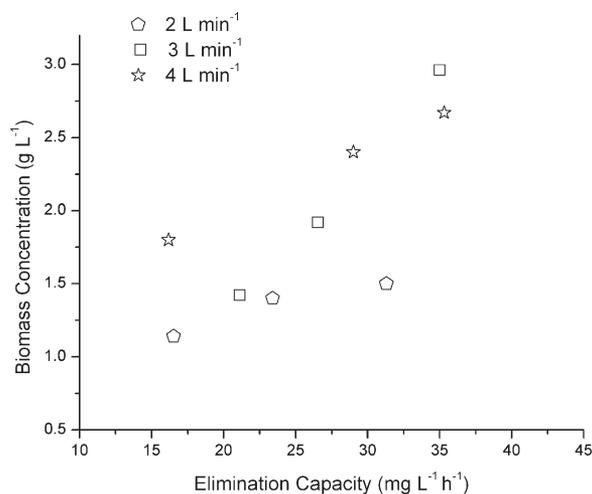


Figure 7. Steady-state biomass concentrations as a function of average EC for the solid–liquid airlift TPPB for varying gas flow rates and loadings.

biotreatment strategies to outperform conventional biotreatment methods. Such strategies include the addition of activated carbon into biofiltration units which can receive a maximum EC of $83.65 \text{ g m}^{-3} \text{ h}^{-1}$ with a RE of 67% for the treatment of BTEX using a mixture of sugar cane bagasse, compost and granulated activated carbon as media (Mathur et al., 2007). In addition, Mohammad et al. (2007) have reported excellent performance for BTEX treatment in mesophilic and thermophilic bioreactors, with a maximum EC of $188 \text{ g m}^{-3} \text{ h}^{-1}$ at a RE of 62% for the mesophilic unit and a maximum EC of $218 \text{ g m}^{-3} \text{ h}^{-1}$ at a RE of 85% for the thermophilic unit. These treatment methods are significantly larger than those obtained in the current study at steady-state, but characterization of these techniques to buffer inlet fluctuations is needed. The steady-state performances of the solid–liquid airlift TPPB at loadings of $60 \text{ g m}^{-3} \text{ h}^{-1}$ are more than 40% lower than the performance of the stirred tank solid–liquid TPPB at the same loading (Littlejohns and Daugulis, 2008a). The performance of an airlift TPPB will also likely be lower than other research for stirred tank TPPBs for compounds such as dichloromethane (Bailon et al., 2009), hexane (Arriaga et al., 2006), toluene (Daugulis and Boudreau, 2008), and benzene (Nielsen et al., 2005b), as these systems were not oxygen or VOC mass transfer limited, and approached 100% RE even at high loadings. However, the solid–liquid airlift TPPB still has the ability to buffer loading fluctuations in the same manner as the stirred tank configurations, and, under optimal operating conditions, has the ability to reduce BTEX concentrations in the off gas significantly. Despite reduced performance at elevated VOC loadings, airlift systems will have a critical advantage over mechanically agitated devices in terms of reduced energy requirement. A preliminary estimate of the energy requirement for the airlift

can be made using Equation (5) (Chisti, 1989).

$$\frac{P_G}{V_{\text{Total}}} = \frac{\rho_L g U_{Gr}}{1 + \frac{A_d}{A_r}} \quad (5)$$

where P_G is the power input (kW), ρ_L the liquid density (g L^{-1}), g the acceleration due to gravity (m s^{-2}), and U_{Gr} is superficial gas velocity in the riser (m s^{-1}). U_{Gr} was determined to be 0.006 m s^{-1} .

A preliminary estimate of the energy requirement for the stirred tank can be made by using Rushton curves that relate the Reynolds number to the Power number for a flat blade turbine (Ruston et al., 1950) and correcting the power for aeration (Ohyama and Endoh, 1955). The conditions used for the calculation of the power input for the stirred tank in Littlejohns and Daugulis (2008a) are an agitation speed of 800 rpm, impeller diameter of 8 cm, and a volumetric gas flow rate of 0.56 L min^{-1} .

Power inputs per unit volume for the airlift and stirred tank are therefore estimated to be 0.019 and 14.7 WL^{-1} , respectively, and thus the energy saved by using the airlift may greatly outweigh a 20% decrease in performance relative to a stirred tank reactor.

Conclusion

During transient operation at a loading of $60 \text{ g m}^{-3} \text{ h}^{-1}$, the polymer-containing airlift TPPB has been shown to have superior performance to a single phase airlift and comparable performance to the liquid–liquid airlift TPPB with silicone oil as the partitioning phase. It was found that for a loading of $20 \text{ g m}^{-3} \text{ h}^{-1}$ there is an optimal performance at a flow rate of 3 L min^{-1} which has a large enough EBRT for sufficient BTEX to transfer out of the gas phase and also a large enough gas flow rate to avoid oxygen limiting conditions. Although performance of the airlift TPPB is lower than the performance of a stirred tank TPPB due largely to mass transfer, the energy input is much larger for the stirred tank, giving the airlift an important advantage.

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