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Oxygen mass transfer and hydrodynamics in a multi-phase airlift bioscrubber system

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ABSTRACT

The addition of select polymer beads to stirred tank bioscrubber systems has been shown to greatly enhance the removal and treatment of toxic VOCs via the capture and sequestration of poorly soluble compounds such as benzene, and the release of these materials, based on equilibrium partitioning, to microorganisms in the aqueous phase. In this study, oxygen volumetric mass transfer coefficients were determined for an 11 L airlift vessel containing tap water alone, tap water with Nylon 6,6 polymer beads (10% v/v), and tap water with silicone rubber beads (10% v/v), over various inlet gas flow rates, with the aim of initially characterizing a low-energy pneumatically agitated reactor (concentric tube airlift). In addition, oxygen transfer rates into the airlift with and without polymers with high oxygen affinity were determined. To further characterize this reactor system, a residence time distribution analysis was completed to determine hydrodynamic parameters including the Peclet number (*Pe*), circulation time (t_c) and mixing time (t_m) over various gas flow rates for the airlift containing tap water with and without silicone rubber. It was found that the addition of silicone rubber beads, which has a high affinity for oxygen, reduced the measured volumetric mass transfer coefficient relative to a system without polymers due to oxygen sorption during the dynamic period of testing, but increased the overall amount of oxygen that was transferred to the system during the dynamic period. The addition of Nylon 6,6, which has very low oxygen uptake, allowed for estimation of the physical effect of solids addition on gas–liquid mass transfer and it was found that there was no effect on the measured volumetric mass transfer coefficient relative to a system without polymers. However, hydrodynamic parameters revealed that the addition of silicone rubber into an airlift vessel improves liquid phase mixing. This investigation has defined key operational features of a low-energy three-phase airlift bioscrubber system for the treatment of toxic VOC substrates.

1. Introduction

Airlift vessels are a useful reactor design due to their simple construction, low-energy requirements and low shear environment (Chisti, 1989). Recently, Littlejohns and Daugulis (2009) examined the performance of a novel airlift solid–liquid two-phase partitioning bioreactor (TPPB) for the treatment of a gaseous mixture of benzene, toluene, ethylbenzene and *o*-xylene (BTEX). The addition of a solid phase, composed of silicone rubber beads, to an airlift bioreactor was shown to increase performance during fluctuating inlet BTEX loadings relative to an airlift without silicone rubber. This was due to silicone rubber absorbing/desorbing BTEX according to achieving equilibrium conditions while meeting metabolic demand, which increased substrate gas–liquid mass transfer and maintained BTEX aqueous phase concentrations at sub-inhibitory levels. However, during this investigation it was found that oxygen mass transfer from the gas to the aqueous phase was the rate limiting step for biodegradation, as dissolved oxygen (DO) reached 0% at average elimination capacities of 31.2 $\mathrm{g\,m^{-3}\,h^{-1}}$ and removal efficiencies of 49.8% during steady-state loadings of 60 $\mathrm{g\,m^{-3}\,h^{-1}}$. In addition, overall system performance of the airlift TPPB was lower in comparison to a stirred tank TPPB treating a BTEX contaminated gas stream whose DO remained over 80% while achieving elimination capacities of 58.5 $\mathrm{g\,m^{-3}\,h^{-1}}$ and removal efficiencies of 97.1% at a steady-state loading of 60 $\mathrm{g\,m^{-3}\,h^{-1}}$ (Littlejohns and Daugulis, 2008).

Characterization of oxygen mass transfer within the airlift TPPB is of interest, as past research has determined that the presence of an immiscible sequestering phase in a mechanically agitated TPPB enhances the oxygen transfer rate (OTR) to the system relative to single phase systems. This has been shown to be the case for a TPPB using the organic solvent, *n*-hexadecane, which has a high affinity for oxygen, as oxygen transfers in parallel from the gas phase to the aqueous/solvent phases which have a higher combined DO saturation concentration (Nielsen et al., 2005). The presence of silicone rubber beads, which also have a high affinity for oxygen, have also provided an increase in OTR in a stirred tank TPPB due to mass transfer in

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series from the gas phase to the aqueous phase, then subsequently from the aqueous phase to the polymer phase (Littlejohns and Daugulis, 2007). In such arrangements, uptake by the polymer increases the gas–aqueous driving force over dynamic periods. This transport in series model is commonly used for gas–aqueous–solid systems in which the suspended solids are larger than the liquid film thickness between the gas and liquid phases (Alper et al., 1980). In addition, it was also demonstrated by Littlejohns and Daugulis (2007) that the addition of polymers in a stirred tank has a physical enhancement effect on oxygen mass transfer. Physical enhancement of gas–liquid mass transfer in three-phase systems has been observed in several studies (Zhang et al., 2006; Ruthiya et al., 2003; Tinge and Drinkenburg, 1995) and is caused by enhanced boundary layer mixing due to turbulence at the gas–liquid interface (Zhang et al., 2006; Ruthiya et al., 2003), resulting in a larger refreshment rate of liquid in the boundary layer by mixing with the bulk fluid. In addition, physical enhancement may involve changes in the gas–liquid interfacial area by coalescence inhibition caused by particles being present at the gas–liquid interface (Ruthiya et al., 2003).

In addition to oxygen mass transfer, hydrodynamic characterization of airlift bioreactors provides important information necessary to describe system performance and facilitate mathematical modeling. In contrast to stirred tank vessels that are assumed to be well-mixed, airlift bioreactors can often have an axial variation of composition, particularly in the downcomer (Chisti, 1989). Hydrodynamic studies have shown that the presence of solids in three-phase systems can have a neutral (Sánchez et al., 2005; Lindert et al., 1992) and positive (Comte et al., 1997; Lu et al., 1995) impact on mixing depending on the reactor geometry, solid size, solid density and solid loading.

Despite the numerous studies on oxygen mass transfer and mixing in three-phase airlift bioreactors, the airlift partitioning bioreactor has not been characterized to date due to the unique physical properties of the solid phase. The purpose of this study was to determine the impact of silicone rubber beads in an airlift reactor on the measured effective volumetric mass transfer coefficient (k_La_{eff}) over a range of air flow rates relative to the k_La_{eff} in an airlift containing solids with low oxygen affinity (Nylon 6,6) and to the volumetric mass transfer coefficient in airlift without solids (k_La). Results were compared to the volumetric mass transfer coefficient of a stirred tank containing silicone rubber, Nylon 6,6 and without solids. The OTR was then determined in the airlift with and without silicone beads to show the true amount of oxygen entering each system. In addition, hydrodynamic characterization was completed for an airlift with and without silicone rubber beads by quantifying Peclet number (Pe), circulation time (t_c) and mixing time (t_m). This work has provided insight into the observed performance of an airlift TPPB for treatment of BTEX contaminated gases in previous work (Littlejohns and Daugulis, 2009). In addition this work has determined the impact of the addition solids with high oxygen affinity on mass transfer and hydrodynamics in an airlift, which had not been undertaken to date.

2. Materials and methods

2.1. Equipment

The reactor used was a 13 L Chemap AG Series 3000 concentric tube airlift fermentor (Männedorf, Switzerland) with dimensions listed in Table 1. All experiments were conducted at $30 \pm 0.1\,^{\circ}\mathrm{C}$ and DO and pH were monitored continuously by probes located at the bottom of the vessel using a Measurement Computing TracerDAQ data acquisition system. Throughout all experimentation, the working volume of the reactor was 11 L with either no solid phase or with 10% v/v polymer beads. The polymer used with a high affinity for oxygen (O_2 diffusivity $= 3.4\times10^{-5}\,\mathrm{cm^2\,s^{-1}}$ (Merkel et al., 2000), O_2 solubility $= 0.18\,\mathrm{cm^3(STP)\,cm^{-3}\,atm}$ (Merkel et al., 2000)) was silicone rubber that was obtained from GE-Mastercraft® in the form of 100% silicone rubber caulking dried to spherically shaped beads (diameter = 2.5 mm). The polymer used with a low affinity for oxygen (O_2 diffusivity $= 1.6\times10^{-9}\,\mathrm{cm^2\,s^{-1}}$ (Jarus et al., 2002), O_2 solubility $= 0.035\,\mathrm{cm^3(STP)\,cm^{-3}\,atm}$ (Weinkauf et al., 1992)) was Nylon 6,6, which was obtained from Dupont Canada (diameter = 2.59 mm). The stirred tank used was described previously (Littlejohns and Daugulis, 2007).

2.2. Oxygen volumetric mass transfer coefficients

k_La for the airlift reactor containing solely tap water was determined for flow rates of 0.03, 0.18, 0.27, 0.36, 0.45 and 0.54 vvm while k_La_{eff} for the airlift containing tap water and 10% v/v silicone rubber beads was determined for flow rates of 0.03, 0.18, 0.27 and 0.361 vvm and k_La_{eff} for the airlift containing tap water and 10% v/v Nylon 6,6 beads was determined for flow rates of 0.27, 0.36, 0.45 and 0.54 vvm. The reason for k_La_{eff} to be not determined over all flow rates is due to the difficulty of fluidizing Nylon 6,6 at low flow rates arising from its slightly higher density than water. Silicone rubber was studied at higher flow rates due to its hydrophobicity and tendency to stay at the gas–liquid interface. The k_La_{eff} and k_La for the stirred tank system were determined at 800 rpm at 0.17, 0.25 and 0.33 vvm in all cases (Littlejohns and Daugulis, 2007).

To determine k_La and k_La_{eff}, the unsteady-state method was used as described by Shuler and Kargi (2002). The vessel was first sparged with nitrogen gas in order to remove all oxygen from the system then air was delivered from a three-hole sparger located at the bottom of the riser column. For consistency, data between 10% and 80% of DO saturation were used for the determination of k_La and k_La_{eff}, according to Eq. (1)

$$\mathrm{OTR} = \frac{dC_L}{dt} = k_La(C_L^* - C_L) \quad \text{or} \quad \frac{dC_L}{dt} = k_La_{eff}(C_L^* - C_L) \tag{1}$$

where C_L is the DO concentration in the liquid phase ($\mathrm{mg\,L^{-1}}$) and C_L^* is the saturation concentration of oxygen in the liquid phase ($\mathrm{mg\,L^{-1}}$). Surface aeration effects were found to be negligible by determining that k_La and k_La_{eff} were much larger when using sparging than without (data not shown). Probe response times were also found to have a negligible effect on k_La and k_La_{eff} over the flow rates used in this study, using an earlier method (Littlejohns and Daugulis, 2007) wherein the probe response time constant was found to be 13.5 s.

Since airlift bioreactors have a concentration profile that is axially distributed, it must be determined if Eq. (1), which assumes the vessel to be well-mixed, is accurate to describe k_La and k_La_{eff} throughout an airlift vessel. Andre et al. (1983) determined k_La using a tanks-in-series model to account for axial distribution and compared it to the k_La obtained using Eq. (1) with a single probe located at the bottom of the airlift vessel. It was found that if Eq. (2) holds true, then Eq. (1) provides an accurate estimate of the k_La determined using the tanks-in-series model,

$$k_La \times t_c \leq 2 \quad \text{or} \quad k_La_{eff} \times t_c \leq 2 \tag{2}$$

where t_c is the circulation time in the airlift (s). Determination of this hydrodynamic parameter will be described in the following section. It was found that the data obtained in this study satisfied Eq. (2), and therefore it is valid to use Eq. (1) to determine k_La and k_La_{eff} in the airlift reactor. This assumption is consistent with other authors who have used a well-mixed model (Eq. (1)) to determine k_La in airlift vessels larger than the one in the current study (Lindert et al., 1992; Freitas and Teixeira, 2001; Guo et al., 1997).

OTR for the airlift with a single aqueous phase only was determined using Eq. (1). For the airlift containing silicone rubber, OTR