Acetate and ammonium diffusivity in membrane-aerated biofilms: improving model predictions using experimental results

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Abstract Membrane-aerated biofilm reactors (MABRs) are advantageous for wastewater treatment because of their ability to achieve both nitrification and denitrification in a single bioreactor. The stratification of membrane aerated biofilms, however, needs to be better understood so that MABRs can be properly designed and implemented. In this study, we present a modified multi-population model that accounts for variation in effective diffusivity in biofilms of variable biomass density. For biofilms grown at a low fluid velocity (2 cm s^{-1}), the variation in effective diffusivity had a profound effect on the predicted stratification and activity of bacterial populations. For biofilms grown at a high fluid velocity (14 cm s^{-1}), biomass density was relatively constant as a function of depth and thus there was less substantial variation in effective diffusivity; our modified model, therefore, predicted a population stratification that was similar to its original version under these conditions.

Keywords Diffusion; membrane aerated biofilm reactors; modeling

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Introduction

Membrane aeration of wastewater treatment bioreactors has several attractive features compared to conventional systems that rely on bubble diffusers. Membrane aeration is bubbleless, which can lead to gas transfer efficiencies approaching 100% (Pankhania *et al.*, 1994) and reduced energy costs. In membrane-aerated bioreactors (MABRs), a unique biofilm grows in which oxygen is provided on the opposite side of the biofilm from the source of nutrients (carbon and nitrogen). Near the membrane, conditions are aerobic and favorable for ammonia oxidation; near the biofilm–liquid interface, conditions are anaerobic and favorable for denitrification. As a result, MABRs can completely remove both carbonaceous and nitrogenous pollutants in a single bioreactor (Semmens *et al.*, 2003).

Previous researchers have reported disparate results on the ability of MABRs to completely remove nitrogenous pollutants. Several researchers have designed membrane-aerated biofilms (MABs) to be fully aerobic such that nitrification proceeded rapidly but denitrification did not occur (Brindle *et al.*, 1998). In contrast, Kappell *et al.* (2005) failed to observe any nitrification during the treatment of a high strength wastewater. The stratification of MABs, therefore, needs to be better understood so that MABRs can be properly designed and implemented.

In our recent research, MABs were mathematically modeled (Shanahan and Semmens, 2004) and experimentally analyzed (Cole *et al.*, 2004) specifically for their ability to simultaneously support both nitrifying and denitrifying bacterial populations. The mathematical model results were generated *a priori*, such that the experimental results could be used to help evaluate many of the fundamental assumptions upon which the model was developed. Herein, we present an initial modification of our multi-population MAB model based upon empirical results. Previously, an average biofilm density and effective

diffusivity were assumed when modeling MABs (Shanahan and Semmens, 2004), although recent research suggests variation in biomass density within MAB structure as a function of depth (Cole *et al.*, 2004). In order to account for this variation, we have used biomass density data to predict the effective diffusivity profiles as a function of depth.

Materials and methods

Biofilm model

A multi-population biofilm model was developed using Aquasim 2.0 software (Wanner and Reichert, 1995) to describe MABs as described previously (Shanahan and Semmens, 2004). The model treats MABs as three compartments connected to each other by diffusive mass transfer links. The membrane is treated as a diffusive link between a well-mixed, gas-filled lumen and the base of a biofilm. Similarly, the diffusive boundary layer is modeled as a diffusive link between the top biofilm layer and the well-mixed, bulk wastewater. Substrate concentrations in both the gas phase and the bulk wastewater were set equal to measured values from the experimental portion of the current research.

Experimental biofilm growth

MABs were grown under well-defined conditions of fluid flow and substrate concentrations in a rectangular closed flow-cell reactor (6 cm wide, 2.5 cm high, 2 m long) as described previously (Cole *et al.*, 2004). Biofilms grew on flat-sheet microporous membranes (20 cm × 1 cm) set into the base of the reactor, flush with the bottom of the tank. For each experiment the reactor was inoculated with 1.0 mL of cryopreserved (15% v/v glycerol) activated sludge from the aeration tanks at the Metropolitan Wastewater Treatment Facility, St. Paul, Minnesota. Reactor feed contained sodium acetate and ammonium chloride dissolved in dechlorinated tap water to achieve the desired substrate concentrations. Following growth, biofilms were removed from the membranes and thin-sliced using a combined cryostat-microtome.

Analytical methods

Chemical oxygen demand and volatile solids concentrations were determined as described in *Standard Methods* (APHA, 1995). Biofilm thickness was determined by the method of Siegrist and Gujer (1985). Biomass concentrations were determined from the biofilm slices as total particulate protein by the method of Lowry *et al.* (1951) using BSA as a protein standard.

Results and discussion

Biomass density varied substantially as a function of depth in a biofilm grown at a fluid velocity of 2 cm s^{-1} (Figure 1). In contrast, biomass density was relatively constant as a function of depth when a biofilm was grown at a fluid velocity of 14 cm s^{-1} (Figure 1). The mean biomass densities of these biofilms were 6.6 g protein L^{-1} and 3.2 g protein L^{-1}, respectively. The volatile solids (VS) concentrations of these two biofilms were 32 g VS L^{-1} and 85 g VS L^{-1}, respectively.

These two biofilms were then modeled as previously described (Shanahan and Semmens, 2004), except that effective diffusivity was assumed to vary as a function of depth. Effective diffusivity profiles were predicted from biomass density profiles by the following equation (Fan *et al.*, 1990):

$$D_{eff} = D\left(1 - \frac{0.43X_f^{0.92}}{11.19 + 0.27X_f^{0.99}}\right)$$

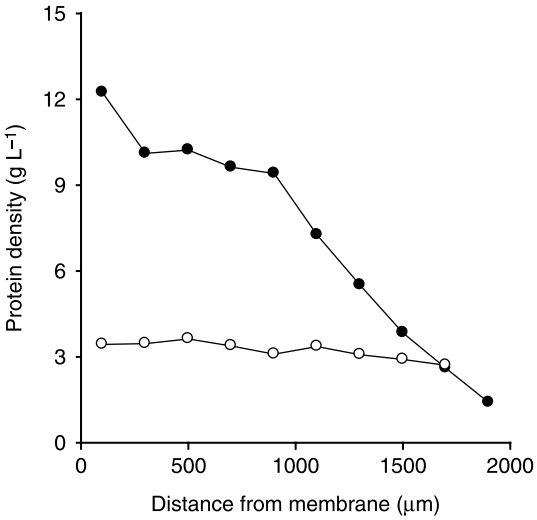

Figure 1 Biomass density as a function of depth in two membrane-aerated biofilms. Solid symbols represent the biofilm grown at a velocity of 2 cm s^{-1}; open symbols represent the biofilm grown at 14 cm s^{-1}

where D_{eff} is the effective diffusivity (m^2 s^{-1}), D is the diffusion coefficient at infinite dilution in water (m^2 s^{-1}), and X_f is the biomass density in the biofilm (g L^{-1}).

For the biofilm grown at a velocity of 2 cm s^{-1}, our original biofilm model predicted that the heterotrophic, nitrifying, denitrifying, and anaerobic bacterial populations would stratify as a function of depth in a membrane aerated biofilm (Figure 2A). Aerobic heterotrophic bacteria were located nearest the membrane, while nitrifying bacteria were found away from the membrane but still in the aerobic portion of the biofilm. Denitrifying bacteria were the dominant population in the middle of the biofilm, while obligate anaerobic populations were found furthest from the membrane. This stratification of bacterial populations is consistent with our empirical observations of membrane aerated biofilms (Cole *et al.*, 2004). Accounting for variation in effective diffusivity, however, had a substantial impact on the profiles of different bacterial populations predicted by our model (Figure 2B). The locations of the aerobic heterotrophic, nitrifying, and denitrifying bacteria all shifted towards the membrane. Aerobic heterotrophic and nitrifying bacteria

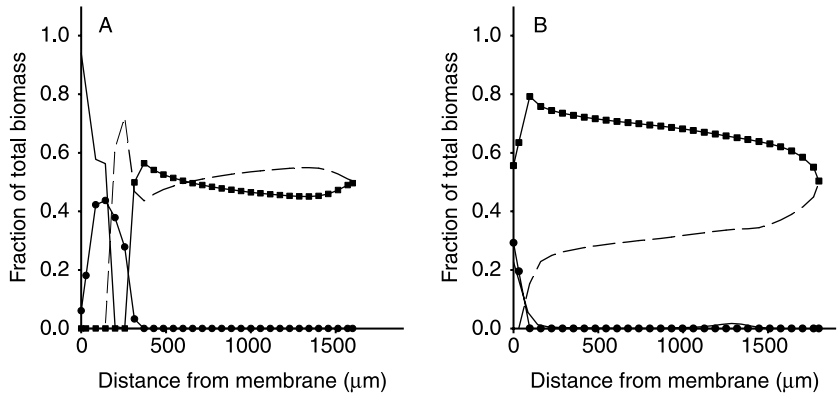

Figure 2 Predicted bacterial population profiles in membrane aerated biofilms grown at 2 cm s^{-1} assuming constant effective diffusivity (A) or variable effective diffusivity (B). Solid lines represent aerobic heterotrophic bacteria; dashed lines represent denitrifying bacteria; solid circles represent nitrifying bacteria; and solid squares represent obligate anaerobic populations

grew only very close to the membrane, whereas denitrifying and obligate anaerobic bacteria were prominent throughout the depth of the biofilm.

For the biofilm grown at a velocity of 14 cm s^{-1}, our original biofilm model again predicted that the heterotrophic, nitrifying, denitrifying, and anaerobic bacterial populations would stratify as a function of depth in a membrane aerated biofilm (Figure 3A). For this biofilm, however, our modified model predicted a less substantial difference in the profiles of pertinent bacterial populations (Figure 3B). The locations of the aerobic heterotrophic, nitrifying, and denitrifying bacteria all shifted slightly towards the membrane such that the obligate anaerobic bacteria were somewhat more prominent.

Variation in the effective diffusivity as a function of depth also had a substantial effect on the predicted respiratory profiles as a function of depth (Figure 4A). Assuming constant effective diffusivity, respiratory activity was predicted to have a hump-shaped profile as a function of depth. This predicted profile of respiratory activity is consistent with our empirical observations of bacterial physiology in membrane aerated biofilms (Cole *et al.*, 2004). In contrast, when variation in effective diffusivity was assumed, then respiratory activity only occurred $<50\,\mu m$ from the membrane. For the biofilm grown at 14 cm s^{-1}, there was only a subtle difference in the respiratory profile when a variation in the effective diffusivity was assumed compared to a constant effective diffusivity (Figure 4B).

There are numerous advantages to using membranes for gas transfer instead of bubble diffusers for wastewater treatment, including lower operating costs and reduced volatile compound emissions (Brindle and Stephenson, 1996). Perhaps the most pertinent advantage is the ability of MABRs to achieve both nitrification and denitrification (Semmens *et al.*, 2003). The design of MABRs, however, is more complex than conventional bioreactor systems in that the proper conditions must be provided to ensure the growth of both nitrifying and denitrifying bacteria. Our mathematical model is currently unique in its ability to predict the stratification of bacterial populations in MABs, and therefore it could become a key tool for the design of MABRs.

The principal limitations of our mathematical model originate with the assumptions that were made *a priori*. In the current paper, we critically evaluate the assumption that effective diffusivity is constant throughout the depth of the biofilm. In our experimental analysis of membrane aerated biofilms, this assumption was reasonable for biofilms grown under high fluid shear but not for those grown under low fluid shear.

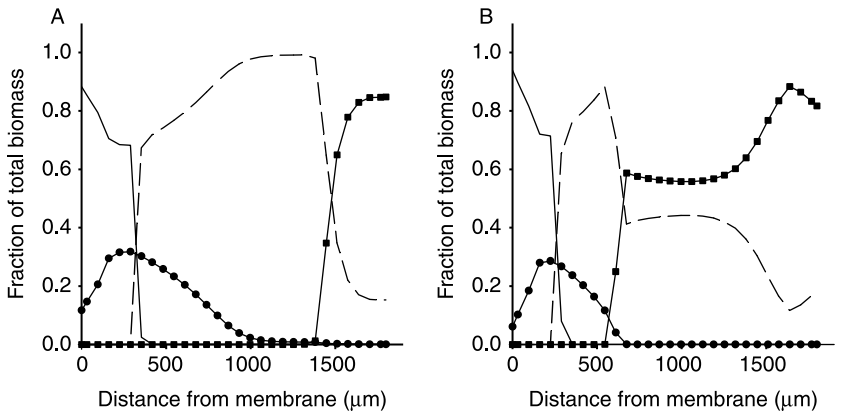

Figure 3 Predicted bacterial population profiles in membrane aerated biofilms grown at 14 cm s^{-1} assuming constant effective diffusivity (A) or variable effective diffusivity (B). Solid lines represent aerobic heterotrophic bacteria; dashed lines represent denitrifying bacteria; solid circles represent nitrifying bacteria; and solid squares represent obligate anaerobic populations

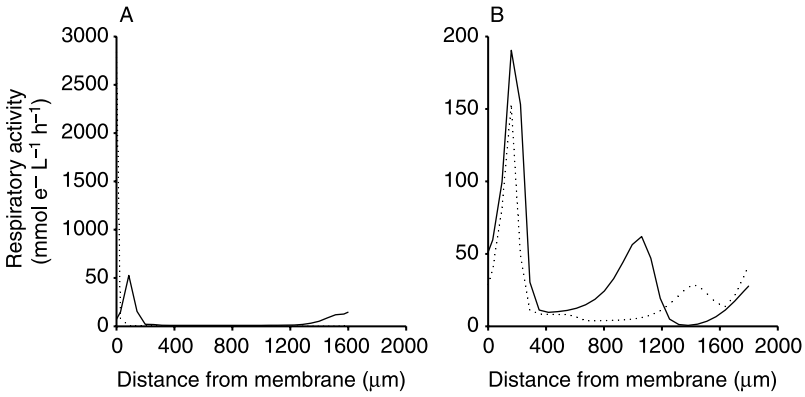

Figure 4 Predicted respiratory activity as a function of depth in membrane aerated biofilms grown at 2 cm s^{-1}. Solid line represents predictions assuming an average biomass density; dotted line represents model predictions assuming variable biomass density

The present study demonstrates that variation in effective diffusivity as a function of depth has a substantial effect on MABs grown at low fluid shear. By accounting for the variation in effective diffusivity that is particularly pertinent at low fluid velocities, our revised model predicts substantial decreases in the quantities of aerobic heterotrophic and nitrifying bacterial populations. Furthermore, the location of respiratory activity shifts towards the membrane, and occurs only in a very thin section of the biofilm. From a practical perspective, this suggests that a substantial fraction of the biomass in low fluid shear biofilms is inactive and merely serves as a diffusional barrier. Furthermore, it suggests that our original model over-predicted the performance of MABRs operated at low fluid shear with respect to their ability to achieve simultaneous nitrification and denitrification.

Conclusions

Our mathematical model of membrane aerated biofilms has been improved by accounting for variation in biomass density, which occurs under low fluid shear. The variation in biomass density had a substantial impact on the stratification of nitrifying and denitrifying bacterial populations, which is a key advantage of using MABRs for wastewater treatment.

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