Multidimensional modeling of biofilm development and fluid dynamics in a hydrogen-based, membrane biofilm reactor (MBfR)

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Abstract

A two-dimensional, particle-based biofilm model coupled with mass transport and computational fluid dynamics was developed to simulate autotrophic denitrification in a spiral-wound membrane biofilm reactor (MBfR), where hydrogen is supplied via hollow-fiber membrane fabric. The spiral-wound configuration consists of alternating layers of plastic spacer net and membrane fabric that create rows of flow channels, with the top and bottom walls comprised of membranes. The transversal filaments of the spacer partially obstruct the channel flow, producing complex mixing and shear patterns that require multidimensional representation. This study investigated the effect of hydrogen and nitrate concentrations, as well as spacer configuration, on biofilm development and denitrification fluxes. The model results indicate that the cavity spacer filaments, which rest on the bottom membranes, cause uneven biofilm growth. Most biofilm resided on the bottom membranes, only in the wake of the filaments where low shear zones formed. In this way, filament configuration may help achieve a desired biofilm thickness. For the conditions tested in this study, the highest nitrate fluxes were attained by minimizing the filament diameter and maximizing the filament spacing. This lowered the shear stress at the top membranes, allowing for more biofilm growth. For the scenarios studied, biomass limitation at the top membranes hindered performance more significantly than diffusion limitation in the thick biofilms at the bottom membranes. The results also highlighted the importance of two-dimensional modeling to capture uneven biofilm growth on a substratum with geometrical complexity.

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1. Introduction

The membrane biofilm reactor (MBfR) is a drinking water and wastewater treatment technology based on membranes that supply a gaseous substrate to biofilm that grows on the membrane exterior (Martin and Nerenberg, 2012). The MBfR has been studied extensively with oxygen/air supporting aerobic processes (Syron and Casey, 2008) and hydrogen gas,
an electron donor, supporting autotrophic denitrification and other reductive bioprocesses (Celmer-Repin et al., 2010; Ergas and Reuss, 2001; Martin and Nerenberg, 2012; Nerenberg and Rittmann, 2004). With complete consumption of hydrogen gas possible within the biofilm layer, hydrogen utilization efficiencies can approach 100 percent (Lee and Rittmann, 2002).

Hydrogen-based denitrification is the application studied in this research.

Among biofilm reactors, MBfRs are unique because of counter-diffusional substrate delivery, where substrates (e.g., hydrogen and nitrate) diffuse into the biofilm from opposing sides. Excessively thick MBfR biofilms can experience dual substrate limitation, where both the inner and outer regions of the biofilm become substrate limited due to diffusional resistance. This results in reduced biological activity and lower nitrate fluxes (Semmens and Essila, 2001). Biofilms with insufficient thickness may also exhibit low nitrate fluxes because of biomass limitation. Considering the sensitivity of the MBfR biofilm to biofilm thickness, biomass management is especially critical to the maintenance of satisfactory denitrification rates. However, difficulty in controlling biofilm detachment makes biomass management the most significant challenge in the scale-up of the MBfR (Syron and Casey, 2008).

Recently, a hydrogen-based MBfR became commercially available for the treatment of nitrate and other oxidized contaminants from compromised drinking water sources (Martin and Nerenberg, 2012). The MBfR module employs a spiral-wound configuration, where layers of inert, plastic spacer net separate layers of hollow-fiber membrane fabric, creating narrow flow channels that guide the water past walls of biofilm-covered fibers. The narrow flow channels provide excellent ratios of membrane surface area to reactor volume. The plastic spacer net partially obstructs the flow channel, producing complex fluid dynamic and mass transport schemes that are highly influential in biofilm development. The spiral-wound configuration is frequently used by filtration modules, such as reverse osmosis (RO) units, and modeling studies have investigated the impact of spacer design on the magnitude and distribution of shear stress and (bio)fouling (Schwinge et al., 2004; Picireanu et al., 2009; Radu et al., 2010). However, the conclusions of these studies are not transferable to MBfR systems. In contrast to filtration systems, the MBfR provides a substrate at the membrane surface and supports biofilms that exhibit unique behavior due to counter-diffusion. It is important to specifically study MBfR biofilm development in the spiral-wound flow channel and the impact of spacer design on biofilm management and contaminant removal fluxes.

Modeling brings an understanding of the biofilm microenvironment (e.g., chemical gradients and structural heterogeneity) and ultimately a better understanding of macroscale process performance (e.g., denitrification fluxes). Furthermore, modeling allows for evaluation of design and operational parameters with the results identifying the most important parameters to explore experimentally. In the past, MBfRs have been modeled by pseudo-analytical (Casey et al., 1999) and one-dimensional (1-d) numerical models (Debus and Wanner, 1992; Downing and Nerenberg, 2008a; Lackner et al., 2008; Pavasant, 1996; Shanahan and Semmens, 2004; Syron and Casey, 2008). However, the spiral-wound MBfR requires multi-dimensional modeling for correct representation. The complex geometry of the woven membrane fabric and spacer net create complicated fluid dynamics and mass transfer patterns that influence biofilm morphology and activity. Moreover, heterogeneity in the biofilm surface morphology (i.e., variability in biofilm thickness) may significantly impact reactor performance, due to the sensitivity of the counter-diffusional biofilm to thickness. There is, however, very limited research addressing the effect of the two-dimensional (2-d) biofilm structure on counter-diffusional biofilms. Matsumoto et al. (2007) simulated the community structure of nitrifying and denitrifying bacteria in an oxygen-based MBfR using a 2-d hybrid approach: small clusters of bacteria were represented as individual entities, and the extracellular polymeric substance was described with a continuum field. For simplicity, however, the model only simulated biofilm growth on a flat surface without consideration of fluid flow and shear patterns.

Cellular automata (CA) models were the first to simulate biofilm growth on a substratum with complicated irregular geometry including packed bed porous media with support grains (Kapellos et al., 2010) and RO feed channels with spacer (Picireanu et al., 2009; Radu et al., 2010). Later, particle-based biofilm models were introduced for biofilms in packed bed porous media (Graf von der Schulenberg et al., 2009; Picireanu et al., 2010; Pintelon et al., 2012). Particle-based representation of the biomass is known to create more realistic biofilm morphology than CA models (Wanner et al., 2006).

The main objective of this study was to develop a 2-d, particle-based biofilm model that simulates a spiral-wound MBfR treating nitrate in drinking water or treated wastewater. An existing 2-d, CA biofilm model used to study biofouling in RO feed channels with spacer (Radu et al., 2010) was modified to accommodate: 1) counter-diffusional biofilm growth on a geometrically complex substratum considering the fluid dynamics and mass transport of multiple substrates and 2) particle-based biofilm representation with biomass attachment, division, spreading and detachment. The model was used to evaluate the effect of substrate concentration and spacer filament configuration on spiral-wound MBfR biofilm development, the biofilm microenvironment, and macroscale reactor performance.

2. Methods

The spiral-wound MBfR model consists of two main parts: 1) a biofilm submodel, which considers biomass as individual rigid spheres undergoing attachment, growth, division, spreading, and detachment and 2) a physical submodel, which calculates hydrodynamics and mass transport with reaction for multiple substrates.

2.1. Model geometry

The spiral-wound MBfR is comprised of alternating layers of woven membrane fabric and spacer net. The longitudinal fibers of the spacer net, oriented parallel to the main flow
direction, separate the layers of membrane fabric and form lanes of flow channels between them. Much thinner transversal fibers, known as filaments, connect the longitudinal fibers at a 90° angle, resulting in a net material (Fig. 1a). The spacer used in the spiral-wound MBR is known as a “cavity spacer” where the transversal filaments rest on the bottom of the flow channel (Schwinge et al., 2002b). The cavities between the filaments become regions of low shear that can foster biofilm growth (Radu et al., 2010).

Significant flow in the transversal direction is not expected since the filaments are oriented orthogonal to the flow, and the filament diameter $d_f$ is much smaller than both the channel height $h_{ch}$ and width. While the longitudinal spacers influence flow and biofilm growth near the outermost edges of the channel, these regions are relatively small (Fig. 1a). Therefore, to avoid large computational difficulties associated with a three-dimensional domain and still maintain key qualitative characteristics of the system, we reduced the problem to 2-d. The curvature of spiral-wound module was also ignored due to the small ratio of $h_{ch}$ to the radius of curvature and the relatively short domain length $l_{ch}$, chosen to save on computational costs (Radu et al., 2010; Ranade and Kumar, 2006). Thus, the 2-d modeling domain became a longitudinal cross-section taken in the middle of a flow channel, as shown in Fig. 1b. The cylindrical hollow-fiber membrane fabric is represented in the cross-sectional view by the series of circles lining the top and bottom boundaries of the channel. The dimensions of the flow channel are based on a preliminary spiral-wound MBR design by APT Water, Inc. (Long Beach, California, USA), the company that commercialized the spiral-wound MBfR. For this study, the spacer geometry was tested by varying $d_f$ and the separation distance between the filaments, known as the mesh length $l_{m}$. Fig. 1b depicts a model channel without biofilm. With biofilm, the channel becomes divided into two subdomains: the biofilm and the bulk liquid. In the bulk liquid there is flow and substrate transport by convection and diffusion. In the biofilm, there is no flow but diffusion and reaction of the substrates.

2.2. Physical submodel

2.2.1. Hydrodynamics

Steady, laminar flow is assumed throughout the channel, with a Reynolds number ($Re$) of approximately 400, and is modeled by the incompressible Navier–Stokes equations (Radu et al., 2010). A fully developed laminar velocity profile is assigned at the inlet, with an average velocity $u_{in} = 0.13$ m/s. As the biofilm develops within the channel, $u_{in}$ at the inlet remains constant. At the outlet boundary, a reference pressure of zero is set. No-slip conditions are assigned to the flow channel walls, designated at the outermost surface (i.e., of spacer, membrane, or biofilm) exposed to the bulk liquid subdomain.

2.2.2. Substrate transport and reaction

Equations for 2-d transport of soluble substrates by convection and diffusion in the bulk liquid are solved (Radu et al., 2010). In the biofilm, substrate balances include diffusion and reaction, with diffusivity of the chemical species assumed as 80% of that in the bulk liquid (Horn and Morgenroth, 2006).

Biomass growth follows dual Monod kinetics (Rittmann and McCarty, 2001) since the concentrations of nitrate $S_{NO_3}$ and hydrogen $S_{H_2}$ can be concurrently rate limiting in counter-diffusion biofilms. The model accounts for active biomass $X_a$ decay and accumulation of inert, undegradable biomass $X_i$. To simplify the model, we chose to neglect the formation of biodegradable decay products, which serve as electron donor for mixotrophic or heterotrophic denitrifying bacteria. This omission is unlikely to significantly change the results or overarching conclusions. The reaction rates and stoichiometry are presented in Table 1.

The transport equations are solved assuming the influent nitrate concentration $S_{NO_3, in}$ is constant and hydrogen is negligible. Since the spiral-wound MBfR typically operates with a high recirculation ratio, the influent and effluent $S_{NO_3}$ values are alike. For this reason, the values of $S_{NO_3, in}$ are similar to expected effluent nitrate concentrations, and the model conditions represent any section of channel within the reactor. At the membrane surface, nitrate flux does not exist, but hydrogen flux $J_{H_2} = \left( \frac{D_{H_2, mem}}{h_{mem}} \right) \left( \frac{p_{H_2, in}}{h_{mem}} - S_{H_2} \right)$, is assigned based on intramembrane hydrogen partial pressure $p_{H_2, in}$, membrane wall thickness $t_{mem}$, hydrogen diffusivity through the membrane $D_{H_2, mem}$, Henry’s law coefficient $H_{H_2}$ and concentration $S_{H_2}$ at the membrane surface.

For both substrates, convective flux is assigned at the liquid outlet boundary. Flux and concentration continuity is assumed at the internal biofilm/liquid boundary.

2.3. Biofilm submodel

The particle-based model describes the formation of a realistic biofilm structure through the mechanistic modeling of biomass attachment, growth, decay, spreading, and detachment. This study considers each biomass particle as a rigid circular entity. The particle-based biofilm model of Kreft et al. (2001) and Picioreanu et al. (2004) was adapted to accommodate biofilm formation on an uneven substratum surface and include biomass attachment and detachment according to the model of Picioreanu et al. (2001). The following sections expand on these modifications.

![Fig. 1 – The model flow channel: a) the 3-d cavity spacer and the b) longitudinal cross-section used as the 2-d modeling domain. In the base case geometry, $l_{ch} = 3.9$ mm and $d_f = 0.44$ mm. Hydrogen is supplied via the membranes as shown on the right side of the figure.](image)
Table 1 – Process matrix.

<table>
<thead>
<tr>
<th>→ component (i)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>Process rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>↓ process (j)</td>
<td>$S_{H_2}$</td>
<td>$S_{NO_3}$</td>
<td>$X_A$</td>
<td>$X_{U}$</td>
<td>$S_{H_2} \cdot K_{H_2} + S_{NO_3} \cdot K_{NO_3}$</td>
</tr>
<tr>
<td>1 Growth of biomass</td>
<td>$-\left(1 \gamma \right)$</td>
<td>$-\left(2.8 - 0.49Y \right)$</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Decay of biomass</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.3.1. Attachment
Initially, 400 particles of active biomass are randomly attached to the filament and membrane surfaces. This allows for relatively even biofilm development. At each subsequent time step, 50 particles are randomly attached to the membrane, spacer material, or biofilm. Reattachment of detached biomass is not considered, though random attachment helps to reseed the biofilm.

2.3.2. Growth and decay
Biomass particles consist of active $X_A$ and inactive $X_U$ biomass components. The mass of each component changes in time according to the rates in Table 1. The model then updates the particle size based on the assigned biomass density $\rho_b$ (Picioreanu et al., 2004; Xavier et al., 2005a). If the decay rate exceeds the growth rate, the particle size decreases.

2.3.3. Division
Once a biomass particle exceeds the maximum allowable diameter $d_{\text{max}}$, it splits into two, with the original mass unevenly distributed (i.e. between 45 and 55%) to avoid synchronized division. To accommodate each other, both new particles shift one radius in opposite directions along a randomly selected angle. To allow for an irregular substratum geometry, we amended the algorithm from Picioreanu et al. (2004): if the shift results in overlap between a particle and domain boundary (i.e., membrane or spacer), a new angle is randomly selected. If none of the chosen angles avoid overlap with the boundaries, the two cells remain partially overlapped until the spreading algorithm eventually separates them.

2.3.4. Spreading
The spreading algorithm (Kreft et al., 2001) redistributes the biomass particles so to minimize overlap with neighboring entities. If a particle is instructed to cross a domain boundary, the particle only moves a percentage of the shift in order to maximize separation with neighbors but still keep the particle within the domain.

2.3.5. Detachment
The biomass detachment function is based on the internal stress of the biofilm induced by the fluid flow and requires the input of mechanical properties of the biofilm, including elastic modulus $E$, Poisson’s ratio $\nu_p$, and cohesion strength $\sigma_{\text{det}}$ (see Section 2.5). The detachment model algorithm is discussed in Picioreanu et al. (2001) and Radu et al. (2010). Briefly, the model simulates two modes of detachment: erosion at the biofilm surface and the sloughing of larger biofilm pieces. Biofilm particles are removed from places where the calculated von Mises stress (equivalent stress, $\sigma$), exceeds $\sigma_{\text{det}}$. If detachment leaves particles unsupported (i.e., floating), they are also removed. Following any detachment step, the fluid dynamics and corresponding stress of the biofilm are recalculated based on the updated biofilm geometry. Using the new $\sigma$ values, the cycle is repeated until no more detachment occurs at that time step.

Detachment highly impacts MBR biofilm development, but is not well characterized (Syron and Casey, 2008). The detachment mechanism of the model required input of the mechanical properties, which are selected based on limited literature (Picioreanu et al., 2001). It is possible the mechanical properties changed with time and/or exposure to shear stress (Ohashi and Harada, 1994; Stoodley et al., 1999). In addition, the model does not directly model reattachment of biomass lost via erosion or sloughing. Instead, at each time step, the model simulates attachment of a set number of particles. In reality, large pieces of sloughed-off biofilm may reattach and clog channels, creating preferential flow channels and variable conditions within the spiral-wound module.

2.4. Model solution
The model solution algorithm is implemented in MATLAB R2009b (Mathworks, Natick, Massachusetts, USA, www.mathworks.com), which calls on the finite element solvers of COMSOL 3.5a (Comsol, Stockholm, Sweden, www.comsol.com) to solve the physical submodel. Since characteristic times for substrate transport are much shorter than those of biofilm growth (Picioreanu et al., 2001), the physical submodel calculates steady state fluid flow and substrate concentrations for each biomass growth step (time interval $\Delta t$). In COMSOL, local biomass concentrations are evaluated by 2-d interpolation of concentrations on a rectangular grid defined by MATLAB. On the same rectangular grid, COMSOL returns the averaged finite element results, including substrate concentrations and internal stress, to MATLAB for use in the biofilm submodel. The basic modeling scheme (Fig. 2) follows the same steps as other models (Graf von der Schulenberg et al., 2009; Picioreanu et al., 2009; Radu et al., 2010), and more detailed explanations can be found in Sections 2.2 and 2.3:
1) Initialization. Both the biofilm and physical submodels are set-up: parameters and initial channel geometry are defined; initial biomass particles are seeded on membrane and spacer surfaces.

2) Physical model: fluid dynamics and substrate transport. A new geometry, resulting from changes in the spatial distribution of biomass, is resolved to a rectangular grid. Subdomain and boundary conditions for fluid flow and substrate transport with reaction are assigned in MATLAB and then solved by COMSOL. Calculated fluid velocity $u$ and substrate concentrations $S_{NO_3}$ and $S_{H_2}$ are passed to MATLAB on a grid. Intermediate results (flow, substrates, biomass) are saved.

3) Biofilm model:
   a. Growth and decay. Based on the local substrate concentrations, the biomass particles change mass and size according to the rate expressions in Table 1.
   b. Division. Biomass particles that reach a maximum diameter divide.
   c. Spreading. A particle-shoving algorithm relocates biomass particles to avoid overlap.
   d. Attachment. A number of particles are randomly attached to biofilm, membrane, or filament surfaces exposed to the bulk liquid.
   e. Detachment. In the new geometry, changed by biofilm development, COMSOL recalculates the fluid dynamics and corresponding mechanical stress in the biofilm. Particles subjected to a stress exceeding $\sigma_{det}$ detach. A new geometry results and COMSOL recalculates fluid dynamics and mechanical stress. This cycle is repeated until no more biomass detaches.

4) Time stepping by $\Delta t$. Steps 2 and 3 are repeated with $\Delta t = 4 \, \text{h}$ until an assigned simulation time is reached. In the simulations tested, a 30-day period was sufficient to reach a quasi-steady state biofilm thickness with $\Delta t = 4 \, \text{h}$.

The simulations were run on the University of Notre Dame Center for Research Computing computational grid using

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometrical parameters</td>
<td>Channel length</td>
<td>$l_{ch}$</td>
<td>23</td>
<td>mm</td>
</tr>
<tr>
<td></td>
<td>Channel height</td>
<td>$h_{ch}$</td>
<td>2</td>
<td>mm</td>
</tr>
<tr>
<td></td>
<td>Separation length between spacer filaments</td>
<td>$l_m$</td>
<td>3.9 (base case)</td>
<td>mm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.9–5.9 (variable)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Diameter of the spacer filaments</td>
<td>$d_f$</td>
<td>0.44 (base case)</td>
<td>mm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.24–0.74 (variable)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Outer diameter of hollow-fiber membrane</td>
<td>$d_{mem}$</td>
<td>0.2</td>
<td>mm</td>
</tr>
<tr>
<td></td>
<td>Thickness of hollow-fiber membrane</td>
<td>$t_{mem}$</td>
<td>0.05</td>
<td>mm</td>
</tr>
<tr>
<td>Operational parameters</td>
<td>Influent velocity</td>
<td>$u_{in}$</td>
<td>0.131</td>
<td>m s$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Nitrate concentration at inlet</td>
<td>$S_{NO_3}$</td>
<td>1–5 (variable)</td>
<td>g N m$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Intra-membrane hydrogen pressure</td>
<td>$p_{H_2}$</td>
<td>70–270 (variable)</td>
<td>kPa</td>
</tr>
<tr>
<td>Physical parameters</td>
<td>Diffusion coefficient of hydrogen in water</td>
<td>$D_{H_2}$</td>
<td>5.11 $10^{-9}$</td>
<td>m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Diffusion coefficient of nitrate in water</td>
<td>$D_{NO_3}$</td>
<td>1.9 $10^{-9}$</td>
<td>m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Ratio of diffusion in biofilm/diffusion in water</td>
<td>$\phi_d$</td>
<td>0.8</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Diffusion coefficient of hydrogen in the membrane material</td>
<td>$D_{H_2,\text{mem}}$</td>
<td>63.7 $10^{-12}$</td>
<td>m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Density of water</td>
<td>$\rho$</td>
<td>997</td>
<td>g m$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Dynamic viscosity of water</td>
<td>$\mu$</td>
<td>8.9 $10^{-3}$</td>
<td>Pa s$^{-1}$</td>
</tr>
</tbody>
</table>
2.6 GHz 4-core processor with 32 Gb of RAM. The computational time for each run averaged 8 days.

2.5. Model parameters

The parameters used in the model are listed in Table 2. The flow channel dimensions and operational parameters are based on a preliminary spiral-wound MBfR design provided by APTwater, Inc. The model tested variable nitrate concentrations at the inlet $S_{NO3}^{in}$ and intramembrane hydrogen pressures $p_{H2}$, with the range of values based on typical operational concentrations for a denitrifying MBfR. Due to high rates of recirculation, $S_{NO3}^{in}$ equals the effluent nitrate concentration, and the EPA regulates nitrate in drinking water.

### Table 2 – (continued)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Henry's law coefficient for hydrogen</td>
<td>$H_{H2}$</td>
<td>65</td>
<td>m$^3$ kPa g$^{-1}$ H$_2$</td>
<td>At 25 °C (Haynes, 2012)</td>
</tr>
<tr>
<td>Elastic modulus of biofilm</td>
<td>$E$</td>
<td>64</td>
<td>Pa</td>
<td>(Picioreanu et al., 2001)</td>
</tr>
<tr>
<td>Poisson's ratio for biofilm</td>
<td>$y_p$</td>
<td>0.3</td>
<td>–</td>
<td>(Picioreanu et al., 2001)</td>
</tr>
<tr>
<td>Threshold stress for biomass detachment</td>
<td>$\sigma_{det}$</td>
<td>3.0</td>
<td>Pa</td>
<td>(Picioreanu et al., 2001) and experimental observations</td>
</tr>
</tbody>
</table>

### Biological parameters

<table>
<thead>
<tr>
<th>Maximum specific rate of substrate utilization</th>
<th>$q_{max}$</th>
<th>1.13</th>
<th>g H$_2$ g$^{-1}$ COD d$^{-1}$</th>
<th>(Rittmann and McCarty, 2001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decay rate</td>
<td>$b$</td>
<td>0.05</td>
<td>d$^{-1}$</td>
<td>(Rittmann and McCarty, 2001)</td>
</tr>
<tr>
<td>Half saturation coefficient</td>
<td>$K_{H2}$</td>
<td>$8 \times 10^{-3}$</td>
<td>g H$_2$ m$^{-3}$</td>
<td>(Lee, 1999)</td>
</tr>
<tr>
<td>Half saturation coefficient</td>
<td>$K_{NO3}$</td>
<td>$70 \times 10^{-3}$</td>
<td>g N m$^{-3}$</td>
<td>(Lee, 1999)</td>
</tr>
<tr>
<td>Biomass yield on hydrogen</td>
<td>$Y$</td>
<td>1.2</td>
<td>g COD g$^{-1}$ H$_2$</td>
<td>(Rittmann and McCarty, 2001)</td>
</tr>
<tr>
<td>Fraction of active biomass that is biodegradable</td>
<td>$f_a$</td>
<td>0.8</td>
<td>–</td>
<td>(Rittmann and McCarty, 2001)</td>
</tr>
<tr>
<td>Biomass particle density</td>
<td>$P_x$</td>
<td>30000</td>
<td>g COD m$^{-3}$</td>
<td>(Rittmann and McCarty, 2001)</td>
</tr>
<tr>
<td>Maximum particle diameter before division</td>
<td>$d_{max}$</td>
<td>9</td>
<td>µm</td>
<td>Chosen</td>
</tr>
<tr>
<td>Number of particles attached each time step</td>
<td>$n_{at}$</td>
<td>50</td>
<td>–</td>
<td>Chosen</td>
</tr>
<tr>
<td>Number of biomass particles initially attached</td>
<td>$n_{at,0}$</td>
<td>400</td>
<td>–</td>
<td>Chosen</td>
</tr>
</tbody>
</table>

### Numerical parameters

| Biomass grid size                                       | $\Delta x$ | 10   | µm                         | Chosen, same in x and y                       |
| Time step for biofilm development                       | $\Delta t$  | 4    | h                           | Chosen                                         |

Fig. 3 – Biofilm development for the base case scenario. The biofilm color indicates biological activity $a$ ranging from 0 to 1. The streamline color represents liquid velocity in m/s. The figures show only part of the larger computational domain, which extended in the x direction from 0 to 23 mm. An animation of this simulation is presented in Supplementary material (Movie 1). To view this figure in color, the reader is referred to the web version of this article.
water to below 10 g N m\(^{-3}\) (USEPA, 2009). The mesh length \(l_m\) and filament diameter \(d_f\) of the spacer were also tested, with the low and high values simulating minimum and maximum values that fit reasonably within the channel dimensions.

The biological and the physical parameters were mostly selected from published studies, though \(D_{H_2,\text{mem}}\) was estimated from gas transfer experiments on dense membranes previously conducted in our lab. For \(\sigma_{\text{det}}\), the selection was based on qualitative observations made of an experimental spiral-wound MBfR and limited literature. Finally, the numerical parameters and maximum size of biomass particles were chosen to achieve reasonable simulation times (days).

2.6. Output analysis

Measures of biofilm development and reactor performance were calculated from the model output. Only the region between the middle of the first and last filaments was taken into account, to exclude inlet/outlet boundary effects. Biological activity \(a\) based on the dual Monod term \(a = \frac{S_{H_2}}{S_{H_2} + K_{H_2}} \cdot \frac{S_{NO_3}}{S_{NO_3} + K_{NO_3}}\), indicates the degree of substrate limitation on biofilm growth and substrate utilization. Activity \(a = 0\) implies no growth, whereas \(a = 1\) implies growth at the maximum rate. Nitrate flux into the biofilm \(J_{NO_3}\) was calculated per projected membrane area. \(J_{NO_3,\text{ss}}\), averaged over multiple time points at quasi-steady state, yielded \(J_{NO_3,\text{ss}}\). Biofilm morphology was also described by average thickness \(L_{\text{avg}}\) and membrane coverage, averaged over the domain at a single point in time.

3. Results and discussion

3.1. Biofilm development

Simulated biofilm development and corresponding changes in flow regime for the base case scenario are shown in Fig. 3. The base case scenario included values of \(S_{NO_3,\text{in}} = 1\) g N m\(^{-3}\), \(p_{H_2} = 170\) kPa, \(l_m = 4\) mm and \(d_f = 0.44\) mm. These values were appropriate for a system treating nitrate from drinking water and are based on input provided by APTwater, Inc.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.watres.2013.04.031.

As expected, the spacer filaments diverted the flow, creating regions of low velocity and vortices behind the filaments and high velocity at the upper membranes. The total amount of biofilm increased until a quasi-steady state was reached, where biofilm growth was roughly balanced by detachment, causing the total amount of biomass to fluctuate

Fig. 4 – Close-up of individual biomass particles growing on the top and bottom membranes (separation between top and bottom not to scale). The selection is outlined by a box in Fig. 3. The colors indicate biological activity \(a\), ranging from 0 to 1. To view this figure in color, the reader is referred to the web version of this article.

Fig. 5 – Biological activity \(a\) and substrate concentrations experienced in the bottom biofilm for the base case scenario at day 30, from \(x = 8–12\) mm along the lower membrane. a) Biological activity \(a\) and fluid velocity \(u\) (m s\(^{-1}\)); b) Nitrate concentration \(S_{NO_3}\) (g N m\(^{-3}\)); c) Hydrogen concentration \(S_{H_2}\) (g H\(_2\) m\(^{-3}\)). To view this figure in color, the reader is referred to the web version of this article.
around an average. This behavior was also predicted in other modeling studies (Radu et al., 2010; Xavier et al., 2005b) and observed experimentally (Ohl et al., 2004). At Day 20, a sloughing event (i.e., detachment of a large piece of biofilm) led to a large loss of biomass in the region between 13 and 14 mm. By Day 30, the biofilm was partially regrown in this region, though additional sloughing events had occurred in other sections of the biofilm. At quasi-steady state, most of the biofilm formed on the bottom membranes, under the protection of filaments. Little biofilm was able to grow on top of the filaments or on the upper membranes due to the high shear stress exerted at these surfaces (Radu et al., 2010; Schwinge et al., 2002b). Fig. 4 provides a close-up of the selection outlined in Fig. 3. Biofilm on the top membranes grew predominantly in the crevices between the hollow-fibers where shear stress was reduced. At each stage of development, the highest biological activity of both the top and bottom biofilms occurred near the outer biofilm surface, indicating that hydrogen was not limiting. Slightly higher activity was observed at the top membranes, since the thinner biofilms experienced less resistance to hydrogen diffusion.

Regions of low shear experienced liquid recirculation (i.e., vortices). Initially, the recirculation zones formed in the wake of the spacers and nearly spanned the gap between the membranes. Biofilm development and the flow were interdependent, and as the biofilm grew, the recirculation regions responded by changing their shape and size. Vortices also developed in the voids formed from biofilm sloughing. Recirculation is known to enhance shear stress and biofilm detachment, compared to a low shear zone without recirculation (Schwinge et al., 2002b). Indeed, at Day 10 it appeared more detachment occurred directly behind the spacers (Fig. 3). Recirculation-based mixing also enhanced local substrate transport to the bottom of biofilm voids, thus increasing the rate of biofilm regrowth in these regions. Fig. 5 presents activity and substrate concentration profiles for a morphologically heterogeneous stretch of biofilm. The voids in the biofilm all experienced recirculation, though the vortex did not reach the bottom of the biofilm for the narrower, leftmost pocket of liquid. Instead, a boundary layer existed directly above the biofilm, and as a result, nitrate was clearly limiting activity as compared to the other two voids.

### 3.2 Effect of substrate concentration

The effect of substrate concentrations on the achievable nitrate flux was evaluated by varying the hydrogen intramembrane pressure $p_{\text{H}_2}$ from 70 to 270 kPa and the nitrate concentration supplied at the inlet $S_{\text{NO}_3,\text{in}}$, from 0.5 to 5 g N m$^{-3}$. Fig. 6 (quasi-steady state flux $J_{\text{NO}_3,\text{ss}}$) and Fig. 7 (2-d activity profiles within the biofilm) reveal the existence of three regimes under different substrate conditions. Firstly, at low influent nitrate concentrations, $S_{\text{NO}_3,\text{in}} = 0.5$ g N m$^{-3}$, the biofilm was nitrate limited and an increase in $p_{\text{H}_2}$ did not improve $J_{\text{NO}_3,\text{ss}}$. In this case, the greatest activity occurred near the biofilm surface, where nitrate was quickly consumed (Fig. 7a). Secondly, at higher values of $S_{\text{NO}_3,\text{in}}$, the biofilm experienced dual substrate limitation, a result of counter-diffusion, where both changes in $S_{\text{NO}_3,\text{in}}$ and $p_{\text{H}_2}$ affected $J_{\text{NO}_3,\text{ss}}$ (Fig. 6). In dual substrate limitation, the biofilm near the liquid becomes hydrogen limited, while the base is nitrate limited. The greatest activity occurs in the middle of the biofilm (Fig. 7b). Finally, $J_{\text{NO}_3,\text{ss}}$ changed very little with $S_{\text{NO}_3,\text{in}}$, but $p_{\text{H}_2}$ had a large effect. In this case, the biofilm was primarily hydrogen limited, with the greatest activity taking place near the hydrogen-supplying membranes (Fig. 7c). These three types of substrate limitation are typical of counter-diffusional biofilms, as described in previous research (Semmens and Essila, 2001). Although not evident from Fig. 6, the improved performance accompanying increased hydrogen pressure experiences diminishing returns.

Many MBfR studies, both modeling and experimental, have stressed the importance of biomass control (Essila et al., 2000; Semmens et al., 2003). Counter-diffusional biofilms have an optimum thickness where the greatest flux is achieved: too thin biofilms may result in low flux due to biomass limitation, whereas excessively thick biofilms can hinder flux due to hydrogen diffusion. To view this figure in color, the reader is referred to the web version of this article.
diffusional resistance. In Fig. 8a, \( J_{NO3} \) is plotted against average biofilm thickness \( L_{f,avg} \) for days 1–30, at the bottom membranes only. Regions of uncovered membrane were not considered in the calculation of \( L_{f,avg} \), so at low coverage, \( L_{f,avg} \) still provided indication of the diffusional resistance introduced by the biofilm. For hydrogen pressure \( p_{HI} = 70 \) kPa, the maximum \( J_{NO3} \) was obtained at an optimum biofilm thickness of approximately 120 \( \mu m \). However, for \( p_{HI} = 170 \) and 270 kPa, high fluxes were achieved over a large range of biofilm thicknesses because diffusional resistance had less impact on \( J_{NO3} \) when hydrogen is abundant (Semmens and Essl, 2001). Moreover, high shear stress conditions maintained \( L_{f,avg} \) below 400 \( \mu m \). Therefore, at the \( p_{HI} \) values tested, biofilm thickness was not an issue for the modeled system.

The nitrate flux \( J_{NO3} \) was very sensitive to membrane coverage. For most scenarios, high coverage of the bottom membranes was quickly established and did not deviate much during the quasi-steady state. However, at \( p_{HI} = 170 \) kPa, an unusually large sloughing event caused a drop in membrane coverage from 93 to 73%. The recovery of \( J_{NO3} \) closely followed the trend of membrane coverage as it dropped and recovered with time, demonstrating the importance of membrane coverage (Fig. 8b). The definition of \( L_{f,avg} \) excluded uncovered membrane, therefore addition of thin, newly recolonized regions slowed the increase of \( L_{f,avg} \) following the sloughing event, though flux was greatly improved. In part, for this reason, similar \( L_{f,avg} \) values supported a range of fluxes (Fig. 8a circled data).

### 3.3. Effect of spacer geometry

The spacer filament geometry influences the performance of the spiral-wound MBR two ways: firstly, it strongly affects channel hydrodynamics and biofilm growth, and secondly, the filaments occupy membrane surface that could otherwise support biofilm and deliver hydrogen. Membrane filtration literature suggests that the most important parameters for spacer design are the orientation of spacer filaments in the flow channel, the ratio of filament diameter to channel height \( d_f/h_{ch} \), and the ratio of mesh length to the channel height \( l_m/h_{ch} \) (Schwinge et al., 2004). For orthogonal filament orientation, this study tested \( d_f/0.24, 0.34, 0.44, 0.54, 0.64, \) and 0.74 mm when \( l_m = 3.9 \) mm and \( l_m = 2.9, 3.9, 4.9, \) and 5.9 mm when \( d_f = 0.44 \) mm. A constant channel height \( h_{ch} = 2 \) mm resulted in \( d_f/h_{ch} = 0.12–0.37 \) and \( l_m/h_{ch} = 1.5–3 \). A channel without filaments was also tested for comparison. The other parameters were held constant at the specified base case conditions.

The spacer configuration impacts the Reynolds number (Re). Studies show that the transition to unsteady flow occurs at higher Re for smaller \( d_f/h_{ch} \) or larger \( l_m/h_{ch} \) ratios (Li et al., 2002). Furthermore, as Re increases, the length of the recirculation region behind a filament is extended (Schwinge et al., 2002a). In this study, Re ranged from 380–475, based on the definition from Schwinge et al. (2002b), who confirmed stability of eddy regions between cavity spacer filaments for \( Re = 90–684 \) (Schwinge et al., 2002a). Under the conditions of this study, the flow remained steady.

#### 3.3.1. Ratio of filament mesh length to channel height \( l_m/h_{ch} \)

Changes in \( l_m/h_{ch} \) altered the distribution of shear as well as the flow recirculation patterns. In Fig. 9, snapshots of the fluid flow and biofilm development are presented without biofilm in the channel and with biofilm growth at quasi-steady state for selected geometries, including a channel without filaments. Of the \( l_m/h_{ch} \) ratios tested, a fully developed recirculation zone spanned the entire gap between the filaments for \( l_m/h_{ch} = 1.5 \) (Fig. 9) and \( l_m/h_{ch} = 2 \). For these cases, the low shear zone remained fairly even in thickness along the bottom membranes. As \( l_m/h_{ch} \) increased, the recirculation zone no longer filled the gap, and the shape of the low shear zone between the filaments increased in asymmetry (Fig. 9, \( l_m/h_{ch} = 3 \)).

The quasi-steady state flux \( J_{NO3,ss} \) at the bottom membrane increased with the \( l_m/h_{ch} \) ratio (Fig. 10c), solely due to the gain in membrane surface area. When \( J_{NO3,ss} \) was expressed in terms of exposed surface area only, the biofilm actually performed slightly worse for increasing \( l_m/h_{ch} \) values. At the top membrane, increases in \( l_m/h_{ch} \) led to better membrane coverage and slightly thicker biofilms (Fig. 10a). Greater separation between filaments lessened the shear stress at the top membranes, allowing for more biofilm growth. Because the

![Fig. 8 - a) Nitrate flux \( J_{NO3} \) as a function of the average biofilm thickness \( L_{f,avg} \) at the bottom membranes for varying hydrogen intramembrane pressures \( p_{HI} \). Circled data highlights a drop in flux that occurred because of a sloughing event. b) Changing biofilm coverage of the bottom membranes and corresponding \( J_{NO3} \), with time. For both a) and b), \( S_{NO3} = 1.25 \) g N m\(^{-3} \), and the base case filament geometry was used.](image-url)
top membrane biofilms were biomass-limited, even such small increases in biomass resulted in large gains in $J_{\text{NO}_3}$ (Fig. 10c).

Without spacer filaments (i.e., $l_m = \infty$ and $d_f = 0$), the shear stress was more evenly distributed between the top and bottom boundaries, and consequently, the reactor achieved more similar biofilm thicknesses $L_{f,ss}$ (Figs. 9 and 10a) and fluxes $J_{\text{NO}_3,ss}$ (Fig. 10c). Of the spacer geometries tested, the best $J_{\text{NO}_3}$ was achieved without filaments. The channel without filaments supported the most biomass growth at the
top membranes, a normally biomass limited region, and the thinnest biofilms at the bottom membranes, where the biofilm faced diffusion limitation. Moreover, lack of filaments made all membrane surfaces available for biofilm growth. Although the best \( J_{\text{NO}_3} \) was achieved in a channel without spacer filaments, the question remains of how to separate the layers of membrane fabric and create channels for liquid flow without a spacer net.

3.3.2. Ratio of filament diameter to channel height \( d_f/h_{ch} \)

At the lower \( d_f/h_{ch} \) ratios tested (i.e., 0.12, 0.17, 0.22), the low shear region took on an asymmetrical shape and recirculation reattached at the membrane surface. At greater \( d_f/h_{ch} \) ratios (i.e., 0.27, 0.32, 0.37), recirculation eventually spanned the entire gap between the filaments. Selected results are shown in Fig. 11. The \( d_f/h_{ch} \) ratio exhibited strong influence on quasi-steady state biofilm thickness \( L_{fs, ss} \). As the ratio increased, thicker biofilms were achieved on the bottom membranes, though biofilm thickness never exceeded the filament diameter. Corresponding biofilm development at the top membranes decreased in both thickness and coverage (Figs. 10b and 11). For increasing \( d_f/h_{ch} \), the flow rate was forced to a narrowing channel, raising shear stress at the top membranes. Consequently, increasing \( d_f/h_{ch} \) resulted in a losses in \( J_{\text{NO}_3} \) at the top membranes, due to biomass limitation, and at the bottom membranes, due to loss in exposed area (Fig. 10d). For this study, a gain in biofilm thickness did not impact \( J_{\text{NO}_3, ss} \) since \( p_{bs} \) was sufficiently high.

3.4. Supporting optimal performance

The modeling results clearly show that biofilm coverage of the membranes is essential to the performance of the spiral-wound MBfR (Fig. 10). The cavity spacer left the top membrane partially uncovered, and therefore underutilized, due to high shear. Better results were achieved with greater filament spacing or smaller filament diameters. For the conditions tested, the simulations suggest the best spacer design should have no filaments at all. The absence of filaments allows for nearly full coverage of both the top and bottom membranes and maintenance of favorable biofilm thicknesses. However, implementation of spacer without filaments remains a question. Other options include placement of spacer filaments at both the top and bottom boundaries to provide symmetrical conditions for biofilm development, or reduction of shear stress at the top wall by lowering the flow velocity or widening the channel. The best spacer design is also highly dependent on the type of wastewater and desired effluent nitrate concentration. Even if the spacer design allows for adequate biofilm growth, major sloughing events can still affect coverage and flux, as shown in Fig. 8. A study of sloughing patterns and their effect on performance would bring important insight into the spiral-wound MBfR performance.

To maintain high nitrate removal fluxes, the biofilm must be thick enough to avoid biomass limitation, but thin enough to prevent excessive mass transfer limitation. Even if an optimal biofilm thickness exists theoretically, it is impossible for the biofilm to be maintained at this value. Furthermore, the optimal thickness changes when source water characteristics and operational parameters fluctuate. The modeling results show that with adequate intramembrane hydrogen pressures, high fluxes are achievable over a range of biofilm thicknesses. When sufficient hydrogen is able to diffuse to the biofilm surface where the nitrate is mainly present, the effect of diffusional resistance is minimized. However, significant amounts of hydrogen could be lost to the bulk liquid after sloughing events or if the hydrogen supply is excessively high. For the conditions tested in this study, biomass limitation was more detrimental to flux than diffusion limitation. For example, at the theoretical optimum, a 100 µm loss in average thickness decreased \( J_{\text{NO}_3} \) by 53%, while a biofilm 100 µm thicker than the optimum encountered a 6% decline in \( J_{\text{NO}_3} \) (Fig. 8, 70 kPa). Therefore, for the conditions tested, the biofilm should be maintained at thicknesses above the theoretical optimum to ensure good performance during operational fluctuations and detachment events.

Spacer design may help to maintain the biofilm thickness within its desirable range. The biofilm morphology predicted

![Fluid streamlines](image)

Fig. 11 – Fluid streamlines, where the color represents the velocity \( u \) and biological activity \( a \) for selected simulations with \( d_f/h_{ch} = 0.12, 0.22 \) and 0.32. The left panels were taken at time 0 and the right panels at quasi-steady state (~30 days). To view this figure in color, the reader is referred to the web version of this article.
by this model closely followed the shape and size of the low shear regions created by the spacers, and biofilm thickness never exceeded the diameter of the spacer. In this way, the spacer design could be used to limit the maximum biofilm thickness.

3.5. Importance of 2-d modeling

One-dimensional MBfR models have been used to demonstrate counter-diffusional biofilm activity or stratification of microbial communities (Downing and Nerenberg, 2008b; Essila et al., 2000; Lackner et al., 2008; Terada et al., 2007). However, multidimensional modeling is required for complicated hydrodynamic and mass transfer regimes where the distribution and extent of biofilm development is otherwise difficult to predict. Furthermore, multidimensional modeling allows for the representation of complex substratum geometries that create niches for biomass growth. For example, the top biofilm grew primarily in the protected spaces between the hollow-fibers (Fig. 4). If a flat membrane surface had been considered, the model would have failed to capture much of the top biofilm that accounted for up to 40% of \( J_{\text{NO}} \) in this situation.

The morphological heterogeneity of the biofilm and geometrical complexity of the substratum are important considerations when predicting substrate fluxes in the MBfR (Wanner et al., 2006). Given the base case geometry with \( S_{\text{NO}} = 2.5 \, \text{g N m}^{-3} \) and \( p_{\text{H2}} = 70 \, \text{kPa} \), the 2-d model estimated a flux around 1.0 \( \text{g N m}^{-2} \text{d}^{-1} \) at the bottom membranes (flux calculation excluded area occupied by spacer filaments) and an average biofilm thickness of 295 \( \mu \text{m} \). Under identical operational conditions, a 1-d, 295 \( \mu \text{m} \) thick biofilm predicted \( J_{\text{NO}} = 0.6 \, \text{g N m}^{-2} \text{d}^{-1} \). A few factors contribute to the discrepancy between the 1-d and 2-d models. Firstly, modeling the curvature of the individual hollow-fibers provides more hydrogen-supplying surface area per length of channel than a flat biofilm. Secondly, rough biofilms experience uneven mass transfer boundary layer thicknesses, which can significantly affect achievable \( J_{\text{NO}} \) (Picioreanu et al., 2000). A 2-d model captures changes in the boundary layer between the peaks and valleys of the biofilm, while a 1-d model does not. Thirdly, a heterogeneous biofilm surface may support greater fluxes through increased biofilm surface area exposed to liquid (e.g., a higher amount of active biofilm is apparent in Fig. 5). However, without formation of recirculation regions in the biofilm valleys, these areas can become substrate limited by increased boundary layer thickness. Finally, MBfR biofilms are counter-diffusional, and the local biofilm thickness can be a determining factor in the achievable substrate flux. The extent of these effects on substrate flux in counter-diffusional biofilms should be studied further.

4. Conclusions

- 2-d models are critical when assessing counter-diffusional biofilms growing on a geometrically complex substratum, like the spiral-wound MBfR. In our studies, spacer filaments unevenly distributed shear stress, leading to uneven distribution of biomass. The biofilm grew primarily in the low shear cavities between the spacers, while the top membranes remained biomass limited. A 1-d model would not capture these effects.
- The spacer design can be used to influence biofilm thickness and location within the flow channel, allowing for improved reactor performance.
- The major factors influencing overall denitrification fluxes are the degree of biofilm coverage and the presence of suitable biofilm accumulation, given the prevalent bulk liquid nitrate concentrations and intramembrane hydrogen pressures.

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