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Model-based comparative performance analysis of membrane aerated biofilm reactor configurations

Eoin Syron and Eoin Casey*

School of Chemical and Bioprocess Engineering, University College Dublin, Ireland

*Corresponding Author: Eoin Casey, School of Chemical and Bioprocess Engineering, Engineering and Material Science Centre, University College Dublin, Dublin 4, Ireland

Email: eoin.casey@ucd.ie
Telephone: +353 1 7161877
Fax: +353 1 7161177
Abstract

The potential of the membrane aerated biofilm reactor for high-rate bio-oxidation was investigated. A reaction-diffusion model was combined with a preliminary hollow-fiber MABR process model to investigate reaction rate limiting regime and to perform comparative analysis on prospective designs and operational parameters. High oxidation fluxes can be attained in the MABR if the intra-membrane oxygen pressure is sufficiently high, however the volumetric oxidation rate is highly dependent on the membrane specific surface area and therefore the maximum performance, in volumetric terms, was achieved in MABRs with relatively thin fibers. The results show that unless the carbon substrate concentration is particularly high, there does not appear to be an advantage to be gained by designing MABRs on the basis of thick biofilms even if oxygen limitations can be overcome.

Key Words:

biofilm, membrane, aeration, model, oxidation

Introduction

The membrane aerated biofilm reactor (MABR), in which oxygen is supplied to the biofilm solely from a gas permeable substratum, shows significant potential as a technology for high-rate biological oxidation. The primary benefit of the MABR is its ability to supply oxygen to the biofilm at elevated pressures, thus potentially overcoming oxygen diffusional limitations while simultaneously maintaining oxygen transfer efficiencies approaching 100%, (Pankhania et al. (1994). Additionally, because the oxygen transfer surface area is constant, the process is insensitive to factors that affect the size and residence time of bubbles, as is the case in conventional aerated bioreactors. Membrane-attached biofilms are different to conventional biofilms in that dual substrate limitation (usually oxygen and the carbon source) can occur as the co-limiting substrates are supplied from the opposing sides of the biofilm, the observed reaction rate is also strongly dependant on the biofilm thickness, (Pavasant et al. (1996). MABRs are also distinguished by microbial population stratification that is favorable for
simultaneous nitrification/denitrification: oxygen concentrations are highest at the biofilm-membrane interface decreasing toward the biofilm-liquid interface where nutrient concentrations are highest, (Cole et al. (2004). This stratification promotes the development of populations of nitrifiers and aerobic heterotrophs adjacent to the membrane, where oxygen is plentiful, and a population of anaerobic denitrifiers adjacent to the liquid where carbon concentrations are highest and oxygen is depleted.

To-date, laboratory and pilot-scale investigations have focused on several application areas, for example, total nitrogen removal (Hibiya et al. (2003), Terada et al. (2006), simultaneous carbonaceous/nitrogen removal (Semmens et al. (2003), Timberlake et al. (1988)), high strength carbonaceous removal and the treatment of volatile organic wastewater constituent (Debus et al. (1994).

In most conventional biofilm based aerobic biotreatment processes the oxygen penetration depth rarely exceeds 100 to 150 μm. Under high carbon-loading rates, biofilm processes can become rate-limited by the oxygen transfer rate and for this reason conventional biofilm technology is generally restricted to low-rate processes, (Nicoletta et al. (2000). The MABR has the potential to fully exploit thick biofilms by using pressurized pure oxygen it overcomes the diffusional limitations, therefore this technology can be expected to find an application for high-rate biotreatment. In order to achieve maximum productivity in the MABR three types of membranes are commonly used; (i) thin microporous membrane modules which promote very high specific surface areas but are unsuitable for thick biofilms. Membrane outer diameters are of the order of several hundred micrometers (ii) non-porous (dense) membrane modules which enable high intra-membrane oxygen pressures and relatively thick biofilms. Membrane outer diameters are of the order of millimeters. (iii) Composite membranes consisting of a microporous structure covered in an outer polymer skin, in general these membranes have outer diameters in the order of several hundred micrometers. The present work focused on the second option because it affords the opportunity to investigate biofilms with active thicknesses greater
than 150μm. In this article the performance limits of a laboratory scale MABR are examined when operating with biofilm thicknesses greater than those considered acceptable for conventional processes. The experimental study is used to validate a mathematical model which is used to compare prospective MABR process configurations. Four selected case studies are modeled with particular consideration to membrane module geometry, biological kinetics, liquid hydrodynamics and biofilm density. This study was undertaken as part of a wider objective to critically examine the potential of the MABR as a viable biotreatment process.

**Materials and methods**

An experimental program was undertaken in order to provide data for validation of a mathematical model which was subsequently employed to examine a number of case studies pertaining to conditions that could be expected in process scale MABRs. Biofilm thickness is a critical parameter in the analysis of MABR performance and accordingly the average thickness was recorded throughout the experimental program. Even after steady state conditions were established, the biofilm thickness did not remain entirely constant due to biological growth, decay and stochastic detachment processes. However, it is possible to investigate aspects of membrane aerated biofilm behavior under pseudo-steady state conditions by taking experimental measurements over timescales that are significantly shorter than the timescale for biofilm thickness increase. The laboratory MABR configuration provides an in situ means of measuring the instantaneous oxygen uptake rate and this together with frequent measurements of average biofilm thickness and carbon substrate concentration in the bulk liquid provided the primary means to validate the model over a range of loading conditions and thicknesses.

**Bioreactor Configuration**

The general scheme of the MABR system used is shown in figure 1. The membrane module consisted of a silicone membrane tube (AlteSil™ Cornwall, UK) of outer diameter 3.0 mm and wall thickness 1
mm with an active length of 1100 mm fitted coaxially in a glass (QVF, Mainz, Germany) of inner diameter 18 mm. The medium was continuously recirculated between the membrane module and a 1000 cm³ stirred-tank reactor (STR) (Bioengineering, Wald, Switzerland) via an “A mount cavity style” gear pump (Cole Parmer, Illinois, USA). The STR was agitated by a single Rushton turbine impeller at 750 rpm. The STR was used for addition of the influent medium stream, removal of the effluent stream, measurement and control of pH, and dissolved oxygen measurement. The pH was measured with a glass type electrode (Mettler Toledo, Leicester, UK). During experiments, the pH of the medium was adjusted to 7.0 by the addition of a concentrated NaOH aqueous solution. The temperature of the system was controlled at 28°C by means of a heating rod in the STR. Nitrogen gas was sparged into the STR at flowrates ranging from 100 to 500 mL min⁻¹ in an attempt to ensure that the only source of oxygen in the system was from the membrane.

Pure oxygen (Air Products, Dublin) with purity > 99.5% was supplied at an elevated pressure (0.2 -0.8 bar gauge) to the membrane lumen. A continuous flow of approximately 5 ml min⁻¹ was maintained to remove any water vapor or gasses which diffuse back into the membrane lumen.

The medium and carbon source (glucose) solutions were fed from separate feed tanks. Both solutions were made up to double strength concentration. They were pumped at equal rates using a Watson Marlow, (Falmouth (Cornwall), UK) 323s pump with dual head, into the bioreactor. No pH adjustment of the medium occurred prior to addition to the reactor.

The feed flow rate was measured by measuring the volume of effluent from the bioreactor over a specific period of time. The reactor headspace was sealed apart from the overflow, through which both the sparged gas and waste medium exited.

**Bacteria and nutrient composition**

The halotolerant acetate-utilizing bacterium, *Vibrio natriegens*, was used in all experiments. The composition of the mineral medium contained is outlined in table I, all reagents were obtained from Sigma (Dublin, Ireland)
**Analytical Methods**

Liquid samples (2ml) were taken at regular intervals and centrifuged to remove all biomass. The supernatant was placed in a clean sample tube and stored in a freezer at -18°C for subsequent analysis.

**Glucose**

All the samples were analyzed using the GOPOD Glucose assay kit from Megazyme (Bray, Ireland). The Megazyme D-Glucose (glucose oxidase / peroxidase; GOPOD) Assay Kit employs high purity glucose oxidase and peroxidase and is used for the specific measurement of D-glucose.

**Total Organic Carbon**

Some of the liquid samples from the bioreactor were also analyzed for TOC using a spectrophotometric based analysis kit LCK, 381 (DR Lange, Berlin, Germany).

**Biomass Concentration**

The optical density of the medium was measured by taking a sample of the liquid and measuring its absorbance at 660nm. The dry weight of a sample of effluent, and the optical density of the effluent at specific time points were measured and a correlation was established.

**Dissolved Oxygen**

The dissolved oxygen of a sample was measured periodically by taking a sample of the effluent and immediately analysing for DO using a Profiline Oxy 197i, oxygen meter (WTW Weilheim, Germany). Nitrogen sparging in the bioreactor occurred continuously to remove only dissolved oxygen. This was done to ensure that there was a minimum of dissolved oxygen in the liquid available for suspended growth.

**Biofilm thickness**

Digital images were taken of the membrane module using a digital camera (Model CAMEDIA C-4000ZOOM, Olympus, Tokyo, Japan) and the images analyzed using, Able image analyzer software (Mu, Labs, Ljubljana, Slovenia).
Images of the membrane-aerated biofilm were taken at regular intervals along the length of membrane module. The overall diameter of the biofilm was then measured at 10 points in each photograph. These measurements were averaged and a biofilm thickness was calculated by subtracting the diameter of the membrane from the measured value. This was done for each photograph along the length of the membrane module. Up to 5 photographs were taken for each time point and the average biofilm thickness was calculated for each time. The accuracy of the measurements was ±30 μm. By using this method of thickness measurement, thickness profiles can be viewed along the length of the membrane module. Measurement of biofilm thickness by this method has the advantage of being non-invasive and non-destructive. The biofilm thickness can vary with length along the membrane module if there is a substrate concentration gradient along the length of the module. However, the flow velocity of liquid through the membrane module used here was 0.18 m/s, giving a mean residence time on each recirculation of 6s, which was sufficient to prevent significant concentration changes along the length of the module from occurring.

**Biofilm Density**

Samples of the tubular membrane covered with biofilm were carefully removed at the end of each run. The dry weight of the total biomass present on the membrane was determined and the average density calculated by dividing the dry weight of biomass by the wet biofilm volume calculated using the average biofilm thickness at the end of each experiment.

**Oxygen transfer rate**

The method has previously been described by Casey et al. (1999). Briefly, needle valves at each end of the membrane module were simultaneously closed, the intra-membrane oxygen pressure was monitored using a pressure transducer (Ps100GC, Sensortechnics, Germany) and recorded on a computer via an Pico log,ADC11 (Picotech, Cambridgeshire, UK). The rate of pressure drop over a defined time period
(120 seconds) was used to calculate the oxygen transfer rate using the equation of state for an ideal gas. The volume inside the membrane between the valves, including the volume of the pressure gauge and fittings, is a known fixed value. The method was validated by measuring the rate of oxygen transferred across the membrane when the reactor was filled with water and the STR off-gas was analyzed using a Servomex 1440D Gas Analyser (Servomex Group Ltd., East Sussex, UK). The water was sparged with nitrogen gas to remove all dissolved oxygen. However a nitrogen concentration driving force exists across the membrane resulting in back diffusion which influences the transient pressure measurement. The oxygen transfer rate (OTR) was calculated from the time dependent pressure measurements, but taking into consideration the nitrogen back diffusion, (Rishell et al. (2004).

Reactors Operation

Before each experiment the reactor was thoroughly cleaned and rinsed with deionised water. The reactor was filled with 1000 ml of fresh medium and inoculated with 50 ml of a 24-hour culture of Vibrio natriegens. The bioreactor was operated in batch mode for 24 hours to allow the growth of sufficient suspended bacteria. During this time the only source of oxygen was via the silicone membrane. After only 24 hours a very thin patchy biofilm was visible on the membrane surface. All initial glucose was consumed, and the reactor was switched to continuous operation with a flow rate of 1000ml h⁻¹. Nitrogen gas sparging began once the reactor was switched to continuous operation. Within 2 days of continuous operation an evenly distributed biofilm had developed on the membrane surface. Significant sloughing, exposing the membrane surface, occurred initially but the regrowth of the biofilm was rapid with complete recovery within 48 hours. After 1 week of operation the amount of sloughing became insignificant and the average biofilm thickness remained steady for a given loading rate.
Mathematical Model

A mathematical model was developed to consider diffusion and reaction of two co-limiting substrates, glucose and oxygen which are supplied from opposite sides of the biofilm. Within the biofilm, molecular diffusion (described by Fick’s Law) and substrate utilization rate (described using Monod kinetics) occur simultaneously. A zeroth order reaction term for glucose uptake was included to account for the ability of *Vibrio natriegens* to degrade glucose via non-oxidative pathways.

Model Assumptions

1. A pseudo-steady state exists, i.e. the timescale for reaction-diffusion is faster than the timescale for biofilm thickness increase.
2. There is no diffusional resistance in the gas side of the membrane.
3. The biofilm is assumed homogeneous and the thickness is uniform along the length of the membrane.
4. The bulk liquid is well mixed and there are no axial gradients along the surface of the biofilm.

Model equations

Combining the reaction rate processes with the steady state mass balances on glucose and oxygen yields the following equations.

\[
\frac{D_{SB}}{d^2O}{dy^2} = \frac{X_{m} \frac{O}{Y_{S/O}}}{K_{O} + O} \cdot \frac{S}{K_{S} + S}
\]

\[
\frac{D_{SB}}{d^2S}{dy^2} = \frac{X_{m} \frac{S}{Y_{S/S}}}{K_{S} + S} \cdot \frac{O}{K_{O} + O} + r_{S,zero}
\]

where $S$ and $O$ are the respective, glucose and oxygen concentrations, and $K_{S}$ and $K_{O}$ are the Monod constants. $D_{SB}$ is the glucose diffusion coefficient in the biofilm, $y$ is the distance in the radial direction, $X$ is the biofilm density and $r_{S,zero}$ is the utilization rate of glucose for non-oxidative metabolism.

Boundary Conditions
The rate of oxygen transferred at the membrane-biofilm interface is assumed to depend on the resistance to mass transfer through the membrane the partial pressure of oxygen in the lumen and the concentration of oxygen at the membrane biofilm interface $O_M$.

$$\frac{dO}{dy}\bigg|_{y=0} = -\frac{k_{MO}}{D_{OB}} \left[ O_M - O_{gas} \right]$$

where $k_{MO}$ is the membrane mass transfer coefficient for oxygen.

The membrane is impermeable to dissolved glucose and the boundary condition for glucose at the membrane is defined as such.

$$\frac{dS}{dy}\bigg|_{y=0} = 0$$

At the biofilm-liquid interface the boundary condition is defined by assuming that the flux on both sides of the biofilm-liquid interface are equal. The boundary condition for glucose at the biofilm liquid interface is:

$$\frac{dS}{dy}\bigg|_{y=L} = \frac{k_L L}{D_S} \left[ S_{BL} - S_L \right]$$

$S_L$ is the glucose concentration in the bulk liquid, and $L$ is the biofilm thickness.

Where $k_L$, the liquid-side mass transfer coefficient, is found from the correlation given by Cote et al. (1989)

$$Sh = 0.0061 Re^{0.363} Sc^{0.333}$$

$$k_L = \frac{D_S Sh}{d_{out}}$$

Oxygen diffusion can also occur across the biofilm liquid interface and here again the flux on both sides is equal

$$\frac{dO}{dy}\bigg|_{y=L} = \frac{k_L L}{D_S} \left[ O_{BL} - O_L \right]$$
OBL and O_L are the oxygen concentrations at the biofilm–liquid interface and in the liquid, respectively. It was assumed in most situations that O_L was equal to zero.

Model numerical solution
The objective of the model is to calculate the reaction rate and nutrient profiles in the biofilm for various intra-membrane oxygen pressures, biofilm thicknesses and glucose concentrations. The equations were first converted to a dimensionless form using the following relationships.

\[
\bar{S} = \frac{S}{S_L} \quad \bar{O} = \frac{O}{O_M} \quad \bar{y} = \frac{y}{L} \quad \beta_s = \frac{S_0}{K_S} \quad \beta_o = \frac{O_0}{K_O}
\]

The dimensionless reaction diffusion equations were then given by

\[
\frac{d^2\bar{S}}{d\bar{y}^2} = \phi_s \frac{\bar{S}}{1 + \beta_s \bar{S}} + \phi_o \bar{O} + \phi_{\text{zero}}
\]

\[
\frac{d^2\bar{O}}{d\bar{y}^2} = \phi_o \frac{\bar{O}}{1 + \beta_o \bar{O}}
\]

\[
\phi_s = \frac{\bar{L}^2 \mu_{\text{max}} X}{Y_{X/S} D_{SB} K_S} \quad \phi_o = \frac{\bar{L}^2 \mu_{\text{max}} X}{Y_{X/O} D_{OB} K_O}
\]

\[
\phi_{\text{zero}} = \frac{\bar{L}^2 q_{S,\text{zero}}}{D_{SB}}
\]

where \( \sqrt{\phi_s} \) = Thiele modulus for carbon substrate, \( \phi_{\text{zero}} \) is the dimensionless zero order reaction rate.

\[\begin{align*}
O &= O_m - Bi_M \frac{dO}{dy} \\
\frac{dS}{dy} &= 0 \\
\frac{dO}{dy} &= -O_i \frac{Bi_L}{S_{\text{bulk,i}}} \\
S &= -\frac{S_{\text{bulk,i}}}{1 + Bi_L}
\end{align*}\]

at \( l = 0 \) \( l = 1 \)

The inverse Biot numbers for oxygen and carbon substrate in the liquid and membrane are given by

\[
Bi_{M,O} = \frac{D_o}{k_o \times \frac{d_{out}}{2}} \quad Bi_{L,O} = \frac{D_o}{k_l \times \frac{d_{out}}{2}} \quad Bi_{L,S} = \frac{D_s}{k_l \times \frac{d_{out}}{2}}
\]

The dimensionless equations and boundary conditions were solved using the boundary value solver in MatLab (MathWorks Inc, Massachusetts, USA). This solver uses a finite difference code that
implements the three-stage Lobatto IIIa formula. This is a collocation formula and the collocation polynomial provides a continuous solution that is fourth order accurate. The model generated the spatial profile of oxygen and carbon substrate in the biofilm for the given parameters. The substrate flux was calculated by measuring the slope of the substrate profile at the liquid side of the biofilm, since the membrane is impermeable to carbon substrate, all substrate entering the biofilm is consumed and the substrate flux equals the substrate utilisation. This is not the case for oxygen as it may pass from the biofilm into the bulk liquid therefore the oxygen flux beside the membrane is equivalent to the oxygen transfer rate.

**Model parameters**

Model parameters are given in table II. The effective diffusivity of a glucose through the biofilm were estimated using the empirical correlation by Fan et al. (1990)

\[
\frac{D_{\text{eff}}}{D} = 1 - \frac{0.43\rho_b^{0.92}}{11.19 + 0.27\rho_b^{0.99}}
\]

\(D\) is the diffusion coefficient of the component in water and \(\rho_b\) is the biofilm density. The diffusion coefficients of the components in water were taken from the literature. The Monod constants were sourced from Linton et al. (1977a). \(\mu_{\text{max}}\) was determined from suspended growth experiments. A yield coefficient of \(Y_{\text{Y}} = 0.5\) kg biomass kg substrate\(^{-1}\) was determined in a batch culture experiments and matches data published by Linton et al. (1977b). Using this value a balanced stoichiometric equation was written to determine the other yield coefficients

\[
C_6H_{12}O_6 + 1.05O_2 \rightarrow 4.13CH_{1.8}O_{0.5} + 1.88CO_2 + 2.28H_2O
\]

This then gives a yield of biomass on oxygen of \(Y_{X/O} = 2.5\) kg biomass kg oxygen\(^{-1}\). The ratio of oxygen to glucose utilization determined for this equation is \(5.36\) g\(\text{sub}\) g\(^{-1}\)\(\text{oxy}\). Assuming that all the oxygen supplied to the membrane is utilized by the membrane-aerated biofilm, the amount of glucose degraded aerobically by the biofilm can be calculated.
**Case Study Analysis**

The numerical model provides the means to examine the effects of biofilm thickness, microbial kinetics, and external mass transfer resistance on the rate controlling processes. However, to make maximum use of the model it was applied to prospective reactor configurations in order to examine the combined effects of reactor design and biofilm properties and operating conditions on overall MABR performance.

In many studies to date, thin microporous membranes have been used to maximize the surface area available for mass transfer and biofilm growth, for example Pankhania et al. (1994). In most of these studies biofilm thickness generally exceed the optimal value and deterioration in reactor performance was observed. An alternative approach is to design the MABR to accommodate thick biofilms, by using high-strength silicone membranes which have the capability to achieve high intra-membrane oxygen pressures and selecting appropriate inter-membrane spacing. Four case studies were selected to examine prospective MABR designs;

*Case I,*

A thin, low density biofilm grown on thin membranes under low liquid velocity

*Case II*

A thin, dense biofilm grown on thin membranes under high liquid velocity

*Case III*

A thick, biofilm grown on large membranes under low liquid velocity

*Case IV*

A thick dense biofilm grown on large membranes under high liquid flow velocity

The reactor characteristics for each case study are shown in table IV where the parameters are calculated assuming a basis volume of the reactor of 1 m$^3$, neglecting any wall effects. For ease of comparison between cases, the same membrane material, silicone, was assumed throughout. In the case
of membrane fibers with large diameters, although the specific surface area is comparatively low, the net concentration of active biomass in the reactor is higher, if oxygen is provided at sufficiently high pressure. The effect of liquid velocity clearly influences the external mass transfer but there is significant body of evidence that velocity also influences the biofilm density, Beyenal and Lewandowski (2000; Pereira et al. (2002), Wasche et al. (2002), therefore in the case studies presented here, a high liquid velocity corresponds to a relatively high biofilm density. Furthermore, it is widely accepted that biofilm density and effective diffusivity are inversely related and the correlation given by Fan et al. (1990) was used to estimate the effective diffusivity from the chosen biofilm densities. The membrane spacing was calculated by setting a minimum distance between adjoining biofilm outer surfaces of 1 mm, this was necessary to ensure adequate contact between the liquid and the biofilm. For each case the reaction-diffusion model was applied using (a) parameters for *Vibrio natriegens* with glucose as carbon substrate and (b) parameters representative of a mixed culture wastewater treatment process, Metcalf & Eddy. et al. (2003). All parameters are shown in table V.

**Results**

**Model validation**

Three components of the total biomass in the reactor system can potentially contribute to glucose utilization; suspended biomass, wall growth and the membrane-aerated biofilm. The only sources of oxygen into the system were though the membrane and from dissolved oxygen in the liquid feed. With the exception of the start-up phase when the membrane-aerated biofilm was thin and inhomogeneous, it was calculated that, in general, the membrane supplied oxygen was completely utilized in the biofilm and did not diffuse into the bulk liquid. It was the objective of this study to minimize wall growth and suspended biomass by sparging nitrogen gas in the STR in an effort to remove any dissolved oxygen from the liquid phase, which may have entered in the feed. However the sparging rate and agitator speed were constrained by the necessity of preventing excessive bubble formation that might contribute to excessive biofilm detachment. Because of this, some dissolved oxygen remained present in the
liquid, typically 0.3 mg L\(^{-1}\), and this supported some wall growth on the glass walls of the STR and membrane module. Model validation was therefore implemented by minimizing the difference between the measured oxygen uptake rate and that predicted by the model.

**Oxygen transfer**

The measured oxygen transfer rate (OTR) was highly dependent upon both the biofilm thickness and the glucose concentration as can be seen in figure 2. It is clear that the OTR increases with increasing glucose concentration. At higher glucose loading rates the active layer within the biofilm expands, not only increasing the reaction rate, but also moving the location of the reaction closer to the membrane and thereby decreasing the diffusional resistance to oxygen in the biofilm (figure 3). With regard to the effect of biofilm thickness it can be seen from model predictions, (figure 4) that the OTR initially increases as the volume of biomass increases. Above the optimal thickness, the OTR declines as biofilm thickness increases due to the increasing diffusional resistance caused by shift in location of active region further from the membrane interface. The optimum biofilm thickness is strongly dependent on the intra-membrane oxygen pressure; in figure 4 the optimum thickness is between 200 and 300 μm for a pressure of 100 kPa.

**Glucose oxidation**

Glucose utilization in *Vibrio natriegens* is used primarily for oxidative metabolism (with the production of biomass and carbon dioxide) and also for product formation, Linton and Musgrave (1983). A carbon balance was performed under several sets of experimental conditions. The rate of glucose converted to products was measured by measuring the concentration of TOC and glucose in the reactor effluent. Since glucose was the only carbon source in the influent medium the difference between the concentrations of TOC and carbon as glucose was equal to the concentration of carbon in the produced products. The products formed when *Vibrio natriegens* grows on glucose include but are
not limited to acetate, acetic acid and ethanol Linton and Musgrave (1983). The experimental measurements of glucose and total soluble products were combined with the stoichiometric equation in order to determine the fraction of supplied carbon directed to biomass, and product formation.

Effectiveness factor analysis

The effectiveness factor \( \eta \) is defined as the observed reaction rate, \( q_{MAB} \) divided by the maximum rate which would be obtained in the absence of diffusional resistance \( q_{MAB,max} \). A high effectiveness factor, therefore, corresponds to a situation where the rate is limited only by the intrinsic kinetics, i.e. the maximum specific growth rate of the microorganism. Lower effectiveness factors are associated with nutrient depletion within the biofilm. Since diffusional limitations are commonly encountered in biofilm systems it is useful to analyse such systems using plots of effectiveness, \( \eta \), against a Thiele modulus \( \phi \),

\[
\eta = \frac{q_{MAB}}{q_{MAB,max}}
\]

\[
\phi_S = \frac{r(S,O)Y_{X/S}L^2}{SD_S}
\]

\[
\phi_O = \frac{r(S,O)Y_{X/O}L^2}{OD_O}
\]

Where \( r(S,O) \) is the rate based on bulk concentration concentrations of S and O.

In the case of dual-limited biofilms it is useful to introduce an additional dimensionless parameter \( \psi \), originally defined by, Karel and Robertson (1987) and represents a ratio describing the relative availability of co-limiting substrates.

\[
\psi = \frac{Y_{X/O}SD_S}{Y_{X/S}OD_O}
\]

External mass transfer has a large effect on the effectiveness factor, showing the importance of minimizing the external resistance to mass transfer. The external resistance to mass transfer is
described by the inverse Biot number (Bi) which is the ratio of external mass transfer to internal mass transfer.

Using the numerical reaction diffusion model the effectiveness factor for Monod kinetics was examined with and without external mass transfer resistance. Values of $\psi$ of 0.05 and 50 were chosen, for illustrative purposes as the upper and lower limits of substrate ratios. There is no significant difference in the effectiveness plots figures 5 & 6 with the inclusion of external mass transfer resistance for the Monod kinetics, this illustrates that for the particular kinetic parameters for *Vibrio natriegens*, the rate of reaction is primarily controlled by oxygen concentration.

At increasing glucose concentrations when $\psi>1$, the system tends towards oxygen limitation and the effectiveness factor with respect to glucose deviates from the solution for zero order kinetics and falls rapidly as shown in figure 5. This can be explained by the fact that the reaction rate is dependent on the value of the Monod constant for oxygen. This is significant because values of the Monod constant for oxygen are difficult to measure it is therefore important to ensure accurate value of $K_O$ when applying biofilm models.

When the effectiveness is examined with respect to oxygen, figure 6, the dependence of reaction rate on oxygen concentration can be seen. The effectiveness begins to drop at a lower value of Thiele modulus than the zero order reaction rate for $\psi<1$ while the effectiveness remains at 1 for $\psi>1$ up to higher values of $\phi_{oxygen}$. Unlike zero order kinetics where the rate is limited by the biomass or the amount of substrate present, with Monod kinetics as the concentration falls close to the Monod constant, the rate becomes dependant upon substrate concentration. For co-limiting substrates Karel and Robertson (1987) defined four substrate limitation regimes; A) Dual limitation where the concentration of both substrates reach zero within the biofilm, B) Oxygen limitation, where the carbon source fully penetrates, C) Carbon substrate limitation, whereby oxygen fully penetrates, D) growth rate limitation, i.e. both substrates fully penetrate the biofilm and reaction rate is limited only by
intrinsic kinetics. In the present study, to distinguish between the four limitation regimes, A to D, the mathematical model was used to define transition boundaries for varying values of \( \psi \) and \( \phi \), whereby limitation was defined according to the concentration of a substrate within the biofilm relative to the value of its Monod constant.

Representative selections of experimental data corresponding to steady-state operation were examined with respect to the zones of limitation, figure 7. It can be seen that for these experimental conditions, glucose limitation was rate controlling.

**Case studies**

For each case, the effect of COD concentration and intra-membrane oxygen pressure on the rate limiting regime can be observed in figure 8. The location of the boundary between zones A to D was calculated using the numerical model for each individual case. Results from the various cases can be compared in Table VI where hydraulic retention time and volumetric removal rates for an arbitrarily chosen COD removal efficiency of 97% with an influent COD concentration of 10,000 mg L\(^{-1}\) are tabulated.

In Case I the biofilm was thin and had a comparatively high effective diffusivity and consequently the reaction rate was limited only by the intrinsic kinetics (zone A) particularly for high COD concentrations. Case II, corresponding to thin biofilms with a comparatively high density give the highest rates of COD utilization, despite the fact that the rate was limited by COD. For cases III and IV, for thick biofilms, despite high oxygen pressures, the Thiele modulus can be seen to remain to the right of the limitation zone intersection for all cases. It can be seen from Table VI that, that although the COD flux remains high (between \(4.15 \times 10^{-7}\) and \(6.91 \times 10^{-7}\) kg m\(^{-2}\) s\(^{-1}\)), the specific surface area is much lower than for cases I and II and therefore the overall COD utilization rate is reduced.
Discussion

MABRs have shown potential for high rate biological oxidation. The work of Yeh and Jenkins (1978) and Brindle et al. (1999) in particular demonstrated the application of this technology to the treatment of high strength wastewater. The analysis of MABR performance is complicated by the fact that co-limiting substrates are supplied from opposite sides of the biofilm and, consequently, the biofilm thickness has a critical effect on overall performance due to the possibility of diffusional limitation. A number of models have been presented in order to aid the understanding the unique nutrient profiles which occur in the MABR, for example, Wanner et al. (1994), Casey et al. (1999) and Essila et al. (2000). Multispecies 1-dimensional modeling has also been examined by Shanahan and Semmens (2004) and Terada et al. (2007). A recent development has been the application of spatially structured biofilm modeling to the MABR Matsumoto et al. (2007). This approach can be useful in the analysis of structure-function relationship and the spatial dynamics of microbial populations in stratified biofilms. However this approach is an emerging development and, at present it is generally accepted that 1-dimensional models are a good compromise between accuracy and numerical complexity for many practical situations, Morgenroth et al. (2004)

Under most of the conditions in experimental work reported here, oxygen limitations were overcome and glucose was the rate limiting substrate. Therefore, the location of maximum activity was generally at or close to the biofilm liquid interface. Under these conditions the nutrient profile within the biofilm is comparable to that of conventional biofilms but, because oxygen was available throughout the biofilm, increases in glucose loading rate did not result in oxygen limitation and the thickness of the aerobically active layer was significantly greater than that in conventional biofilms, Essila et al. (2000). The numerical model developed here is unique in that it allows generation of reaction rate regime plots, such as figure 7, which can be used to examine the effect of key parameters on the transition between the four rate-limiting regimes encountered in membrane attached biofilms. Once transition boundaries have been determined using the numerical model for a given set of kinetic parameters, a plot of log $\psi$ is
versus log φ allows determination of the limiting factors. Biofilm thickness (L) is incorporated in φ and the effects of variations in thickness are easily observed from these plots. Thick biofilms have a high dimensionless reaction rate φ >> 1 and under these conditions the biofilm is usually limited by nutrient diffusion. A reduction in φ therefore brings the system closer to optimum performance.

**Case Studies**

The case studies were chosen to illustrate MABR performance trends across a range of practically achievable operating parameters. The performance characteristics predicted by the model assume idealized conditions including the absence of axial gradients and homogeneous biofilm and most importantly the assumption of steady-state conditions. It is clear that practical implementation on MABR technology at process scale must overcome several scale-up and operational challenges, not least biofilm thickness control and it seems likely that steady-state operation is not attainable. However, one of the objectives of this study was to appraise the relative merits of possible MABR configurations in an effort to provide guidance on the future research directions for this technology and therefore the assumption of pseudo-steady state conditions was applied.

Cases I and II (thin membranes), are comparable with the experimental studies reported by Brindle et al. (1999) and Pankhania et al. (1999) in terms of membrane module design. The predicted COD volumetric removal rates vary between 17.6 and 59 kg m⁻³ d⁻¹ depending on the assumed biofilm density for the mixed culture biofilm. Brindle et al (1999) reported rates of up to 28.7 kg m⁻³ d⁻¹ for an influent COD concentration of 2400 mg L⁻¹, a HRT of 1.8 hr and a removal efficiency of 90%. These figures suggest that the model parameters are reasonably consistent with those that can be expected in practice.

It is clearly desirable for bioreactors to operate with high biomass concentrations. In the case of biofilm reactors this can be achieved either by aiming for a high substratum specific surface area or, alternatively, by permitting thick biofilms. The latter option is only feasible if diffusional limitations do
not reduce the active biomass concentration; the MABR is perhaps the only technology that can exploit this option. Excessively thick biofilms are problematic in all biofilm processes and are particularly problematic in hollow-fiber MABRs where they can cause channeling and decrease the working volume of the reactor, Semmens et al. (2003).

One of the objectives of this study was to investigate if thick biofilms could be exploited for the oxidation of high strength wastewater, given that the MABR uniquely provides the means to overcome oxygen limitation in such systems. The results of the case studies presented here suggest that, unless the COD concentration is particularly high, there does not appear to be an advantage to be gained by designing MABRs on the basis of thick biofilms even if oxygen limitation can be overcome. There seems to be some potential in MABR configurations where the specific surface area and the biofilm density can be maximized, as in Case II. However, maintaining a thin dense biofilm could prove to be a major operational problem and would clearly require effective thickness control, and well mixed turbulent conditions to promote a dense biofilm. The liquid pumping requirements can be expected to result in considerable energy requirements.

**Conclusions**

Four distinct rate limiting regimes can be identified for the MABR. In order to aid comparative analysis of various MABR designs and operational modes, a reaction-diffusion model was developed which generated reaction regime plots in terms of dimensionless parameters. An experimental program, involving a single-tube hollow fiber MABR, was undertaken to validate the model and it was found that carbon-substrate limitation predominated. A preliminary MABR process model was developed in order to provide quantitative performance analysis of a number of prospective hollow-fiber based MABR process options with particular application for high-rate COD removal. Cases studies were chosen with kinetic, operational and design parameter ranges to reflect values that the MABR is likely
to encounter in full-scale wastewater treatment applications. The model was applied to investigate if thick biofilms could be exploited for the oxidation of high strength wastewater, given that the MABR uniquely provides the means to overcome oxygen limitation in such systems. It appears that, unless the COD concentration is particularly high, there does not appear to be an advantage to be gained by designing MABRs on the basis of thick biofilms even if oxygen limitations can be overcome. High COD removal fluxes can be attained, however the volumetric removal rate is highly dependent on the membrane specific surface area and therefore MABR designs with relatively thin membranes would be appear to be superior for high volumetric oxidation rates.
**Nomenclature**

**Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>d</td>
<td>Diameter (m)</td>
</tr>
<tr>
<td>k</td>
<td>Mass transfer coefficient (m s$^{-1}$)</td>
</tr>
<tr>
<td>q</td>
<td>Specific reaction rate (s$^{-1}$)</td>
</tr>
<tr>
<td>r</td>
<td>Volumetric reaction rate (kg m$^{-3}$ s$^{-1}$)</td>
</tr>
<tr>
<td>y</td>
<td>Distance in radial direction (m)</td>
</tr>
<tr>
<td>S</td>
<td>Concentration of Substrate (kg m$^{-3}$)</td>
</tr>
<tr>
<td>O</td>
<td>Concentration of Oxygen (kg m$^{-3}$)</td>
</tr>
<tr>
<td>D</td>
<td>Diffusivity (m$^2$ s$^{-1}$)</td>
</tr>
<tr>
<td>K</td>
<td>Monod constant (kg m$^{-3}$)</td>
</tr>
<tr>
<td>L</td>
<td>Biofilm thickness (m)</td>
</tr>
<tr>
<td>$Y_{x/s}$</td>
<td>Yield of biomass on substrate (g biomass g substrate$^{-1}$)</td>
</tr>
<tr>
<td>$Y_{x/o}$</td>
<td>Yield of biomass on oxygen (g biomass g oxygen$^{-1}$)</td>
</tr>
<tr>
<td>X</td>
<td>Biomass concentration (kg m$^{-3}$)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density (kg m$^{-3}$)</td>
</tr>
<tr>
<td>$\mu_{\text{max}}$</td>
<td>Maximum specific growth rate (s$^{-1}$)</td>
</tr>
</tbody>
</table>

**Subscripts**

- **cal**: Calculated
- **eff**: Effective
- **O**: Oxygen
out  outer diameter

S  Carbon substrate

M  Membrane

B  Biofilm

L  Liquid

MAB  Membrane aerated biofilm

zero  Zero order reaction

**Dimensionless numbers**

Bi  Biot number

Re  Reynolds number

Sc  Schmidt number

Sh  Sherwood number

$\sqrt{\phi}$  Thiele modulus

$\beta$  Dimensionless Monod constant

$\eta$  Effectiveness factor

$\psi$  Relative availability of substrates
References


Figure Legends

Figure 1: Schematic of reactor layout

Figure 2. Comparison between experimental OTR and predicted OTR using reaction diffusion model for biofilm thickness and varying substrate concentrations, ● 0.05 kg m\(^{-3}\), ○ 0.1 kg m\(^{-3}\), ▼ 0.31 kg m\(^{-3}\)

Figure 3. Predicted response of OTR for given biofilm thickness 1000μm to varying carbon substrate concentration, at constant oxygen pressures (115, 130, 160, 200) kPa absolute,

Figure 4. Predicted response of OTR for an oxygen pressure of 100kPa gauge to varying biofilm thickness, at constant substrate concentrations (0.01, 0.025, 0.05, 0.075, 0.1, 0.25, 0.5, 1)gL\(^{-1}\).

Figure 5. Effectiveness factor for \(\psi=50\), \(\psi = 1\), \(\psi = 0.05\), for both \(\rightarrow\) zero order kinetics (-----) and Monod kinetics calculated using steady state model, with respect to substrate for a) no external resistance b) external resistance on both sides, with Bi\(_O=0.1\) and Bi\(_L=0.05\)

Figure 6. Effectiveness factor for \(\psi=50\), \(\psi = 1\), \(\psi = 0.05\), for both \(\rightarrow\) zero order kinetics (-----) and Monod kinetics calculated using steady state matlab model, with respect to oxygen for a) no external resistance b) external resistance on both sides, with Bi\(_O=0.1\) and Bi\(_L=0.05\)

Figure 7. Plot of zones of limitation a) dual limitation b) oxygen limitation c) substrate limitation d) growth rate limitation, ● Experimental data

Figure 8. Identification of reaction rate regime for 4 Case studies under varying substrate-loading conditions, COD=0.01 - 1 gL\(^{-1}\), \(P_O= 20-300\)kPa.
**Table I: Medium Composition**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>23.4 gl⁻¹</td>
</tr>
<tr>
<td>EDTA</td>
<td>0.1 gl⁻¹</td>
</tr>
<tr>
<td>Trace element solution (Alawadhi et al. (1990))</td>
<td>0.5ml l⁻¹</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>0.4 gl⁻¹</td>
</tr>
<tr>
<td>Na₂HPO₄·2H₂O</td>
<td>1.4 gl⁻¹</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>0.7gl⁻¹</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>0.1 gl⁻¹</td>
</tr>
<tr>
<td>CaCl₂·2H₂O</td>
<td>0.1 gl⁻¹</td>
</tr>
<tr>
<td>Parameter</td>
<td>Value</td>
</tr>
<tr>
<td>-----------</td>
<td>---------</td>
</tr>
<tr>
<td>$K_S$</td>
<td>0.03</td>
</tr>
<tr>
<td>$K_O$</td>
<td>0.005</td>
</tr>
<tr>
<td>$D_S$</td>
<td>6.7×10$^{-10}$</td>
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<tr>
<td>$D_O$</td>
<td>2.9×10$^{-9}$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>42</td>
</tr>
<tr>
<td>$D_{eff}$</td>
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</tr>
<tr>
<td>$Y_{XS}$</td>
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</tr>
<tr>
<td>$Y_{X/O}$</td>
<td>2.5</td>
</tr>
<tr>
<td>$r_{S,n}$</td>
<td>1.1×10$^{-4}$</td>
</tr>
<tr>
<td>$\mu_m$</td>
<td>4×10$^{-4}$</td>
</tr>
<tr>
<td>$k_{MO}$</td>
<td>7×10$^{-6}$</td>
</tr>
<tr>
<td>$k_{LS}$</td>
<td>Correlation</td>
</tr>
<tr>
<td>HRT (hr⁻¹)</td>
<td>Carbon supplied (kg carbon s⁻¹)</td>
</tr>
<tr>
<td>------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>0.12</td>
<td>$4.36 \times 10^7$</td>
</tr>
<tr>
<td>0.23</td>
<td>$2.52 \times 10^7$</td>
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<tr>
<td>0.45</td>
<td>$6.08 \times 10^8$</td>
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<tr>
<td>0.84</td>
<td>$7.62 \times 10^8$</td>
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</table>

Table III Carbon balance for selected values of HRT.
Table IV Specification of model reactors for case studies

<table>
<thead>
<tr>
<th>Case</th>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane outer diameter (mm)</td>
<td></td>
<td>0.3</td>
<td>0.3</td>
<td>5</td>
<td>5</td>
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<tr>
<td>Membrane wall thickness (mm)</td>
<td></td>
<td>0.1</td>
<td>0.1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Specific surface area (m² m⁻³)</td>
<td>739</td>
<td>739</td>
<td>277</td>
<td>277</td>
<td></td>
</tr>
<tr>
<td>Packing density (kg m⁻³)</td>
<td></td>
<td>0.055</td>
<td>0.055</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td>Average biofilm density (kg m⁻³)</td>
<td>10</td>
<td>40</td>
<td>10</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Average biofilm thickness (μm)</td>
<td>200</td>
<td>200</td>
<td>1000</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Net biomass concentration (kg m⁻³)</td>
<td>1.23</td>
<td>4.92</td>
<td>3.32</td>
<td>13.3</td>
<td></td>
</tr>
<tr>
<td>Effective diffusivity (m)</td>
<td></td>
<td>0.74</td>
<td>0.41</td>
<td>0.74</td>
<td>0.41</td>
</tr>
<tr>
<td>Wetted perimeter (m)</td>
<td></td>
<td>235</td>
<td>235</td>
<td>88</td>
<td>88</td>
</tr>
<tr>
<td>Area available for flow (m²)</td>
<td></td>
<td>0.94</td>
<td>0.94</td>
<td>0.65</td>
<td>0.65</td>
</tr>
<tr>
<td>Effective diameter (m)</td>
<td>4.02×10⁻³</td>
<td>4.02×10⁻³</td>
<td>7.41×10⁻³</td>
<td>7.41×10⁻³</td>
<td></td>
</tr>
<tr>
<td>Liquid velocity (m s⁻¹)</td>
<td></td>
<td>0.1</td>
<td>0.5</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Reynolds number</td>
<td></td>
<td>402</td>
<td>2008</td>
<td>741</td>
<td>3707</td>
</tr>
<tr>
<td></td>
<td>Vibrio natriegens</td>
<td>Mixed culture</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>-------------------</td>
<td>---------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_{\text{max}}$ (day$^{-1}$)</td>
<td>23.3</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_a$ (kg m$^{-3}$)</td>
<td>0.03</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_o$ (kg m$^{-3}$)</td>
<td>0.005</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Y_{x/s}$ (kg biomass kg$^{-1}$ substrate)</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Y_{x/o}$ (kg biomass kg$^{-1}$ substrate)</td>
<td>2.5</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table VI  Results of Case studies for both *Vibrio natriegens* and for the mixed culture

<table>
<thead>
<tr>
<th></th>
<th><strong>Vibrio natriegens</strong></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Case</td>
<td>I</td>
<td>II</td>
<td>III</td>
</tr>
<tr>
<td>COD flux</td>
<td>kg m(^{-2}) s(^{-1})</td>
<td>1.19x10(^{-6})</td>
<td>2.64x10(^{-6})</td>
<td>1.48x10(^{-6})</td>
</tr>
<tr>
<td>HRT (97%) removal</td>
<td>hr</td>
<td>3.06</td>
<td>1.38</td>
<td>6.56</td>
</tr>
<tr>
<td>COD Loading</td>
<td>kg m(^{-3}) day(^{-1})</td>
<td>74.0</td>
<td>164</td>
<td>23.0</td>
</tr>
<tr>
<td>COD Removal</td>
<td>kg m(^{-3}) day(^{-1})</td>
<td>71.0</td>
<td>159</td>
<td>23.0</td>
</tr>
</tbody>
</table>

|                  | **Mixed culture**      |        |        |        |
|                  | Case                   | I      | II     | III    | IV     |
| COD flux         | kg m\(^{-2}\) s\(^{-1}\) | 2.92x10\(^{-7}\) | 9.78x10\(^{-7}\) | 6.91x10\(^{-7}\) | 4.15x10\(^{-7}\) |
| HRT (97%) removal| hr                     | 12.5   | 3.73   | 14.1   | 23.5   |
| COD Loading      | kg m\(^{-3}\) day\(^{-1}\) | 18.1   | 60.8   | 11.1   | 6.69   |
| COD Removal      | kg m\(^{-3}\) day\(^{-1}\) | 17.6   | 59.0   | 10.8   | 6.49   |