Microbial Enhancement of TCE and 1,2-DCA Solute Flux in UF-Membrane Bioreactors

Subbalaxmi Inguva, Melissa Boensch, and Gina S. Shreve
Dept. of Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202

An ultrafiltration membrane process was used to remove and biograde chlorinated aliphatic hydrocarbons trichloroethylene (TCE) and 1,2-dichloroethane (1,2-DCA) from dilute aqueous streams. The effect of microbial biodegradative activity on TCE and 1,2-DCA solute flux in a polypropylene membrane was examined using microbial strains Pseudomonas cepacia $PR1_{31}$ for the biodegradation of TCE and Xanthobacter autotrophicus GJ10 for the biodegradation of 1,2-DCA. Initial experiments were conducted in diaphragm cells in the absence of microorganisms to determine the diffusion coefficient of 1,2-DCA and TCE in the polypropylene ultrafiltration (UF) membranes. The diffusivities were 4.7×10^{-8} cm^2/s for 1,2-DCA and 1.41×10^{-7} cm^2/s for TCE. Subsequent experiments were conducted with microorganisms on the permeate side to examine the effect of microbial degradation of 1,2-DCA and TCE on the solute flux across the UF membrane. Experiments were conducted sequentially in batch and flow diaphragm cells and then in a hollow-fiber UF module to systematically examine the effect of microbial activity on the solute flux in each configuration and the ability of mathematical models to predict the microbial enhancement of solute flux. Microbial biodegradation of TCE and 1,2-DCA significantly enhanced the solute flux, and experimental results were correlated with steady- and nonsteady-state solute component balance models for the flow and batch diaphragm cells, respectively. Model and experimental results agree well. Implications for using membrane bioreactors to treat CAH contaminated groundwater and industrial effluents are discussed, as well as a method for examining the effect of biological reaction on membrane transport processes.

Introduction

Chlorinated aliphatic hydrocarbons are produced industrially in large amounts for use as solvents, cleaning agents, and chemical intermediates. The persistence of chlorinated aliphatic hydrocarbons (CAHs) in the environment has resulted in the pollution of aquifers, surface waters, and soils (Bouwer et al., 1986). Perchloroethylene (PCE), dichloroethane (DCA), and trichloroethylene (TCE) are among the seven most commonly found contaminants in groundwater or drinking-water supplies (Clark et al., 1984). Recent developments in ultrafiltration (UF) membrane separation techniques demonstrate the effectiveness of membrane processes for treatment of wastewater and groundwaters containing CAHs. Pervaporative removal of chloroform, 1,2-DCA, and chlorobenzene utilizing UF membranes has been demonstrated to be effective for solute concentrations in the parts per million (ppm) to parts per billion range (Zhu et al., 1983). Solvent extraction of methylene chloride, 1,2-DCA, chloroform, trichloroethane, TCE, and benzene from dilute aqueous streams utilizing UF membranes has also been shown to be effective (Hutter et al., 1994). While pervaporation and solvent extraction accomplish the concentration of the CAH contaminants resulting in permeates requiring subsequent disposal or destruction, the objective of biological removal is the production of a contaminant-free permeate stream requiring no subsequent treatment.

Environmental applications of UF membrane bioreactors have been studied by several researchers. The presence of the UF membrane prevents the microbial cells from entering the treated stream, thus preventing potential complications

Correspondence concerning this article should be addressed to G. S. Shreve.

in downstream treatments where the presence of introduced microorganisms may be undesirable. Choi et al. (1992) studied the biodegradation of benzene, xylene, and toluene in a membrane bioreactor in which the solute diffused through silicone tubing and was biodegraded on the permeate side. Livingston (1993a) demonstrated 98.5% removal of phenol from a synthetic wastewater in a membrane bioreactor with an influent concentration of 1,000 ppm at low flow rates of 18 mL/L. Livingston also demonstrated removal of chloronitrobenzene from industrial wastewater using a membrane bioreactor (1993b). The performance of membrane bioreactors for removal and degradation of CAHs and, in particular, solute fluxes, which are practically obtainable in these systems, has been limited. One previous study of a UF membrane bioreactor for TCE degradation concluded that microbial activity may enhance solute mass transfer and that the phenomena of microbial enhancement of solute fluxes in UF membrane bioreactors should be further investigated (Aziz et al., 1995).

The studies described here utilize a batch-stirred diaphragm cell with a flat-sheet polypropylene UF membrane to evaluate solute fluxes and to calculate solute removal efficiencies. Microorganisms on the permeate side of the membrane degrade 1,2-DCA as a primary substrate or TCE as a cometabolic substrate. The resulting solute depletion on the permeate side establishes a concentration gradient that drives solute diffusion across the membrane. The membrane diaphragm cells were designed to measure the enhancement of solute flux due to microbial degradation of 1,2-DCA and TCE, as well as the upper limit of 1,2-DCA and TCE solute fluxes, which may be practically obtainable in membrane bioreactors. The microbial enhancement of CAH fluxes in the membrane bioreactor were examined in a steady-state flow diaphragm cell and then in a hollow-fiber membrane bioreactor in order to systematically examine the magnitude of the microbial enhancement of solute flux, first in simple and then progressively more complex and industrially applicable flow configurations, along with the ability of mathematical models to predict the performance of these UF membrane units. Quantitation of the microbial enhancement of solute flux provides an indication of the magnitude by which biological reactions can enhance the performance of UF membrane processes. Such results are important for comparison of membrane bioreactors with existing pervaporation and solvent extraction techniques, as well as for the design of future generations of membrane bioreactors utilizing alternative reaction-driven separation strategies.

The research was carried out in four progressive experimental studies. Initially the overall mass-transfer coefficient of 1,2-DCA and TCE in the membrane batch diaphragm cell was evaluated at varying stir rates. These data were used to calculate the diffusivity of 1,2-DCA and TCE in the UF membrane. In addition, a batch diaphragm cell was used to determine the solute flux across the membrane in the presence and absence of microbial biodegradation of solute on the permeate side. Microbial degradation kinetics of TCE and 1,2-DCA were determined in separate batch experiments that are described elsewhere (Inguva, 1997). The CAH solute flux in the presence of microbial degradation of CAH averaged approximately twofold greater than those obtained in the absence of microbial degradation of solute. In the third group of studies solute flux and removal rates were measured in a continuous stirred diaphragm flow cell. The magnitude of the solute flux in the presence of microbial reaction was approximately 65% greater than that obtained without reaction. Finally, the solute flux and removal rate of 1,2-DCA was evaluated in the hollow-fiber membrane bioreactor. The overall mass-transfer coefficient for the hollow-fiber module was determined in abiotic experiments prior to the measurement 1,2-DCA solute flux in the presence of microorganisms. Steady- and nonsteady-state mass-balance models were developed for the flow and batch membrane bioreactors, respectively. With the exception of the hollow-fiber bioreactor the magnitude of solute-flux enhancement obtained experimentally is in good agreement with that predicted by the mathematical models.

Materials and Methods

Quantitative analysis of TCE and 1,2-DCA

TCE and 1,2-DCA concentrations were measured by gas chromatography (GC). Aqueous samples were either extracted with hexane or applied directly to a Perkin-Elmer (PE) HS-40 Headspace Analyzer interfaced with a Perkin-Elmer Autosystem GC equipped with an electron capture detector (ECD). The method of analysis was based on EPA Method 8010A. A DB-5 MS capillary column of 0.32 mm ID obtained from J&W Scientific was used with helium as the carrier gas at 1.5 mL/min and nitrogen as the makeup gas at 38.5 mL/min. 1,2-DCA extractions were performed by adding a 0.5-mL aqueous sample to 2 mL of hexane in a 4-mL Teflon stoppered vial. The vial was gently vortexed, then mixed on a Specimix for approximately 15 min. The hexane extract was further diluted 1:4 in hexane prior to GC analysis. TCE concentrations in the aqueous phase were measured by a similar extraction procedure, except that 0.5 mL of the aqueous TCE sample was extracted with 3 mL of hexane prior to further 1:4 dilution in hexane and analysis on the GC. Head-space analysis of the aqueous samples required fifteenfold dilution of TCE samples and tenfold dilution of 1,2-DCA samples in water prior to GC analysis to ensure that concentrations were in the linear response region of the ECD.

Measurement of microbial biomass

Microbial biomass was determined by measurement of cell-protein concentration using the Lowry method, with bovine serum albumin as the protein standard (Lowry et al., 1951). An Hitachi U-2000 UV/VIS spectrophotometer was used to measure the absorbance at 750-nm wavelength for *Xanthobacter autotrophicus* GJ10 and at 500-nm wavelength for *Pseudomonas cepacia* $PR1_{31}$. Protein assays were performed on cells in either modified mineral media with vitamins (Van den Wjingard et al., 1993) or basal-salts biological media (Shields and Reagin, 1992). A correlation between protein concentration and cell number was established by plate counts on TNA plates (Olsen and Shipley, 1973).

Measurement of TCE and 1,2-DCA flux and diffusivity in batch diaphragm cells

Stirred batch diaphragm cells and a stirred flow cell were used to evaluate the mass-transfer coefficients of 1,2-DCA

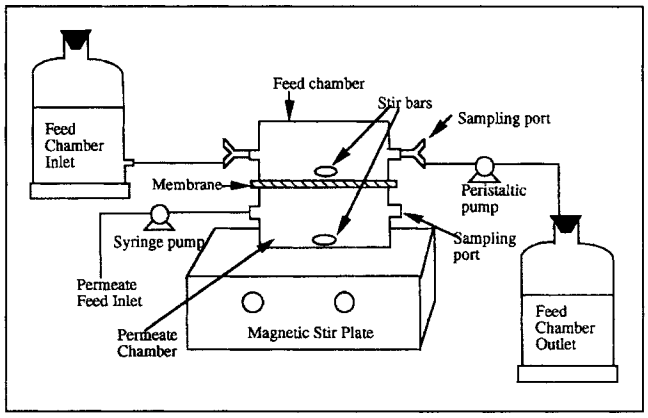

Figure 1. Stirred diaphragm cell.

and TCE in the ultrafiltration membrane as a function of stirring rate and to estimate the diffusivity of 1,2-DCA and TCE in the Metricel membrane. All batch and flow diaphragm cell experiments utilized the Metricel (Cat. No. M5PU047) polypropylene membrane manufactured by Gelman Sciences. Metricel membranes with a pore size of 0.1 μm and a thickness of 89 μm were obtained in 47-mm discs for the batch diaphragm studies (Figure 1). The batch cell consists of two glass cells, each 35 mL in volume, separated by the UF membrane. Initial concentrations of 120 ppm 1,2-DCA or 40 ppm TCE were added to the upper chamber and microbial media were added to the lower chamber. Both cells were magnetically stirred at varying rates, which were previously determined using a stroboscopic method. Triplicate samples were removed from the upper and lower chambers until the system reached equilibrium. Sampling intervals ranged from 6 min to 15 min, and the experiments typically lasted from 30 min to 150 min. Inert glass beads were added to the lower chamber to maintain the liquid contact with the membrane surface. The flow diaphragm cell solute mass-transfer experiments were performed similarly, except that the inlet and outlet lines were clamped off, allowing no flow. The cells were magnetically stirred at predetermined rates, and triplicate samples were removed from the upper and lower chambers at equal time intervals until equilibrium was reached. Data from the batch and flow diaphragm cells were analyzed together to confirm that the mass-transfer properties of the batch and flow diaphragm cells were the same.

Mathematical modeling of the batch diaphragm cell

A mathematical model was developed to verify experimental results and to interpret the solute-flux enhancement in the presence of microbial activity. Equations 1 and 2 were derived from an unsteady solute component balance across a small axial volume element of the membrane assuming (1) pseudo-steady-state flux across the membrane, (2) constant solute diffusivity, and (3) well-mixed components. The rate of contaminant removal on the feed side was determined from a solute component balance on the feed chamber:

$$\frac{dC_f}{dt} = -\frac{1}{V_t} jA. \tag{1}$$

The net rate of contaminant removal on the permeate side was determined from a solute component balance on the permeate chamber, which includes the solute flux through the membrane and the biological reaction rate:

$$\frac{dC_p}{dt} = \frac{1}{V_b} jA + R_a. \tag{2}$$

The biological reaction rate was described using the following nonlinear biodegradation rate law:

$$R_a = -\frac{kC_pX}{K_s + C_p}. \tag{3}$$

A cell balance on the permeate side yields Eq. 4, describing the change in microbial biomass:

$$\frac{dX}{dt} = \mu X \tag{4}$$

The solute flux across the membrane can be described as

$$j = K_0(C_f - C_p), \tag{5}$$

where

$$\frac{1}{K_0} = \frac{1}{k_{f_{\text{feed}}}} + \frac{1}{\frac{D_m}{\delta}} + \frac{1}{k_{f_{\text{permeate}}}} \tag{6}$$

for the stirred diaphragm cells.

Experimentally measured mass-transfer coefficients and kinetic rate constants were then used in the model for solute flux in the presence of biological reaction. Equations 1 through 5 were solved for the case with reaction using the ordinary differential equation solver function of Polymath, distributed by CACHE of Austin, TX.

Evaluation of solute flux and removal rate in the batch diaphragm cell with microbial reaction

The influence of biological reaction on the solute flux across the polypropylene membrane was examined in batch diaphragm cell experiments in the presence of the microbial degradation of the solute. In these studies the upper and lower chambers of the diaphragm cell were autoclaved. Sterile stock solutions of the solute in biological media were added to the upper chamber. The lower chamber of the diaphragm cell was then filled with microbial cells. Adsorption of solute by the microorganisms was previously determined to be negligible (Inguva, 1997). TCE and 1,2-DCA concentrations were monitored in both the upper and lower chambers and a mass balance was used to determine the microbial removal rate and substrate flux across the membrane. The experiment was performed in duplicate with an accompanying abiotic control to enable calculation of physical losses and the overall mass-transfer coefficient. The flux enhancement ratio was calculated as the ratio of the solute flux obtained in the biological system to that in the abiotic system:

$$\text{Flux enhancement ratio} = \frac{(j)_{\text{biological reaction}}}{(j)_{\text{no reaction, abiotic}}}. \quad (7)$$

The solute removal efficiency in the system was calculated from an overall material balance as

$$\%\,\text{Removal} = \left\{1 - \frac{[V_f(C_f)_{t=t}] + [V_b(C_p)_{t=t}]}{(V_f(C_f)_{t=0})}\right\} \times 100. \quad (8)$$

Continuous studies in the flow diaphragm cell

The design of the flow diaphragm cell is similar to that of the batch diaphragm cell, with the presence of inlet and outlet streams to the feed and permeate chambers (Figure 1). Sterile stock solutions of the solute in biological media were pumped through the top feed chamber by a peristaltic pump. Media containing no solute were pumped through the bottom permeate chamber by a syringe pump. TCE and 1,2-DCA concentrations were measured at the upper and lower chamber outlets to determine when steady state was achieved. These experiments were conducted with and without cells in the permeate chamber. Experiments conducted in the absence of microorganisms were used to estimate physical losses, the overall mass-transfer coefficient, and to calculate the solute flux in the absence of microbial degradation of solute. Experiments conducted with microorganisms were used to calculate the removal efficiency and solute flux in the presence of a biological reaction.

Mathematical modeling of the flow diaphragm cell

A mathematical model was developed to verify the experimental results and to interpret the solute flux enhancement due to microbial activity. The mathematical model describing the startup period of the flow-cell operation was derived from an unsteady-state solute component balance around the top and bottom chambers of the stirred flow cell, assuming (1) a pseudo-steady-state flux across the membrane, (2) inlet and outlet flow rates across the chamber are equal, and (3) both compartments are well mixed. The rate of contaminant transport across the membrane in the stirred flow cell can then be described as

$$\frac{dC_f}{dt} = [Q_f(C_{f_0} - C_f) - AK_0(C_f - C_p)]/V. \quad (9)$$

An unsteady-state solute component balance on the permeate side, assuming that no solute was present in the inlet stream and the amount of solute in the membrane is negligible relative to the total quantity in the system, results in Eq. 10:

$$\frac{dC_p}{dt} = [K_0A(C_f - C_p) - Q_pC_p - R_aV]/V \quad (10)$$

where the biological reaction rate is described by Eq. 3. The change in biomass in the 1,2-DCA experiments is described by Eq. 4. The cell balance does not account for cell removal in the permeate, since the microbial growth rate was much larger than the microbial removal rate in the very slow permeate flow rates. Experimentally measured mass-transfer coefficients and kinetic rate constants were also used in this model. The equations were solved using Polymath.

The logarithmic concentration difference was used to calculate the transmembrane flux from the following equation:

$$\text{Flux} = j = K_0(\Delta C)_{\ln}. \quad (11)$$

The flux enhancement ratio was calculated from Eq. 7. The overall removal efficiency was calculated from a mass balance over the reactor system and is expressed as % removal defined by Eq. 12:

$$\%\,\text{Removal} = 100\left(1 - \frac{(Q_fC_f + Q_pC_p)}{Q_fC_{f_0}}\right). \quad (12)$$

Abiotic and biological experiments were conducted for both model compounds under identical flow, stir rate, and other operation conditions. The feed to the permeate side of the reactor consisted of biological media containing no solute in the abiotic experiments. Solute fluxes obtained in the presence of biological reaction were used to calculate the flux enhancement due to microbial activity and the solute removal efficiency.

Determination of overall mass-transfer coefficient and solute flux in the hollow-fiber bioreactor

The overall mass-transfer coefficient, solute flux enhancement due to biological reaction, and the 1,2-DCA removal efficiency were examined in a hollow-fiber membrane bioreactor (Figure 2). The hollow-fiber module was manufactured by Microgon (Catalog No. CG2M-020-01N) and contained a Celgas polypropylene membrane. This reactor configuration was chosen for its high surface area per unit volume ratio and is a single-pass shell and tube unit. The module shell, with endcaps composed of polysulfone and polyurethane potting material, was constructed by the Wayne State University Glass Shop. A sterile sample feed solution was prepared by adding measured quantities of 1,2-DCA to sterile biological

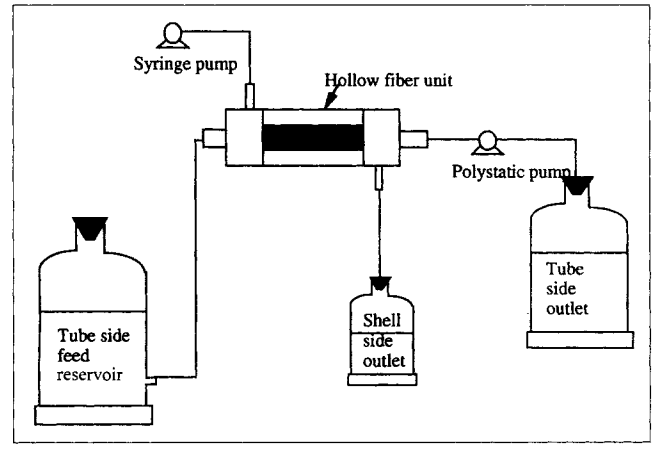

Figure 2. Hollow-fiber membrane bioreactor.

media in a well-stoppered Erlenmeyer flask. The feed was pumped through the tube side of the hollow-fiber unit. A sterile biological medium containing no solute was simultaneously pumped through the shell side of the hollow-fiber unit. The reactor was inoculated on the shell side with a solution of approximately 10^7 *X. autotrophicus* GJ10 cells per milliliter. 1,2-DCA concentrations were measured by sampling the outlet streams at measured time intervals to determine when steady state was achieved. Outlet solute concentrations were used to evaluate overall removal rates at steady state. Cell density was monitored by protein concentration measurements. The overall aqueous flow rate through the lumen side was maintained at 0.563 mL/min, and the flow through the shell side of the reactor was maintained at 4.34 mL/h. Experiments were conducted with biological reaction and without microorganisms, under identical operational conditions and, in particular, flow rate.

Mathematical modeling of the hollow-fiber membrane bioreactor

A simple mathematical model was developed to evaluate the solute removal efficiency and the effect of microbial action on the solute flux. The transport equations were derived from a mass balance across a small axial volume element of hollow-fiber reactor. The conditions and assumptions applied in the derivation of these equations are (1) steady-state conditions; (2) constant solute diffusivity and density; (3) plug-flow conditions; and (4) negligible axial diffusion. Mass transfer across the membrane in a single hollow fiber can be described by the following equation resulting from a component balance across a small axial volume element of the tube:

$$\frac{dC_f}{dz} = \frac{\pi K_0 d_{it}(C_f - C_p)}{Q_f}. \tag{13}$$

A component balance on a small axial volume element on the shell side reflecting the solute transfer across the membrane into the shell, and solute removal by biological reaction is given by Eq. 14 when the shell-side feed stream does not contain solute:

$$\frac{dC_p}{dz} = \frac{\pi K_0 d_{it} N(C_f - C_p) - R_a A_s}{Q_p}. \tag{14}$$

The nonlinear rate equation was again used to describe the biological reaction rate (Eq. 3). The solute mass transfer across the membrane was described by Eq. 11.

Assuming a local equilibrium at the membrane–aqueous interface, the steady-state flux can again be calculated from the overall mass-transfer coefficient and the logarithmic mean concentration difference described in Eq. 11. This relationship can be used to experimentally determine the overall mass-transfer coefficient K_0 (Yun et al., 1992). A solute component balance was used to derive a similar expression for the overall mass-transfer coefficient in the abiotic hollow-fiber module system:

$$K_0 = Q_f \frac{(C_{f_0} - C_{f_e})A}{(\Delta C_{\ln})}. \tag{15}$$

The abiotic experiments in the hollow-fiber module were conducted to determine the overall aqueous-phase mass-transfer coefficient (K_0). The solute transmembrane flux in the presence of biological reaction was calculated using Eq. 11; the solute flux enhancement ratio, using Eq. 7; and the overall removal efficiency, from Eq. 8.

Results and Discussion

Diffusion coefficient of 1,2-DCA and TCE in the UF membrane

Solute fluxes obtained in the batch diaphragm cell flux and diffusivity studies were used to determine the overall mass-transfer coefficient from Eq. 5. The diffusion coefficient of 1,2-DCA and TCE in the Metricel membrane was determined from the y-intercept value of a linearized plot of the correlation developed for predicting mass-transfer coefficients in stirred UF membrane diaphragm cells (Colton, 1969). The data were fit to the linearized form of the referenced correlation (Eq. 16) and plotted to find the solute diffusivity in the membrane from the y-intercept value (Figures 3 and 4):

$$k_f = 0.0443 \frac{D_{AB}}{d} \left(\frac{\nu}{D_{AB}}\right)^{1/3} \left(\frac{\omega d^2}{\nu}\right)^{0.75}. \tag{16}$$

The relative error associated with the triplicate experimental concentration measurements and with the calculation of the mass-transfer coefficient was calculated (McCracken, 1988) and is shown in Figures 2 and 3. The diffusion coefficient of 1,2-DCA in the Metricel membrane is estimated from the y-intercept to be 4.7×10^{-8} cm^2/s (Figure 3). The diffusion coefficient of TCE in the Metricel membrane may be similarly estimated to be 1.41×10^{-7} cm^2/s (Figure 4). This value is somewhat lower than values previously determined experimentally for the diffusivity of TCE in water and oil (Hutter et al., 1994) and air (Zander et al., 1989), ranging from a low value of 9.3×10^{-6} cm^2/s in water to 8.26×10^{-2} cm^2/s in air.

Microbial enhancement of TCE and 1,2-DCA solute flux and removal efficiency in the batch diaphragm cell

Solute flux and removal efficiencies were evaluated at a low and a high solute concentration for both TCE and 1,2-DCA. In experiments where volatile losses were significant the mass balance model (Eqs. 1 and 2) was corrected for physical losses from the feed and permeate chambers, respectively, using the rate of volatilization and loss determined for the same time intervals in the abiotic experiment. This correction was significant for later time points of the TCE experiments, since TCE is the more volatile of the two solutes. Therefore, early time points were used for calculation of the solute flux enhancement ratio, prior to significant volatile losses. It is observed from the experimental data that 1,2-DCA was completely degraded in about 10 to 15 h, and TCE was degraded completely within 6 h at 3.6 ppm TCE. At the high TCE concentration (21.5 ppm) solute degradation was only 70%, which may be due to decreased viability of the resting *P. cepacia* $PR1_{31}$ in the batch systems.

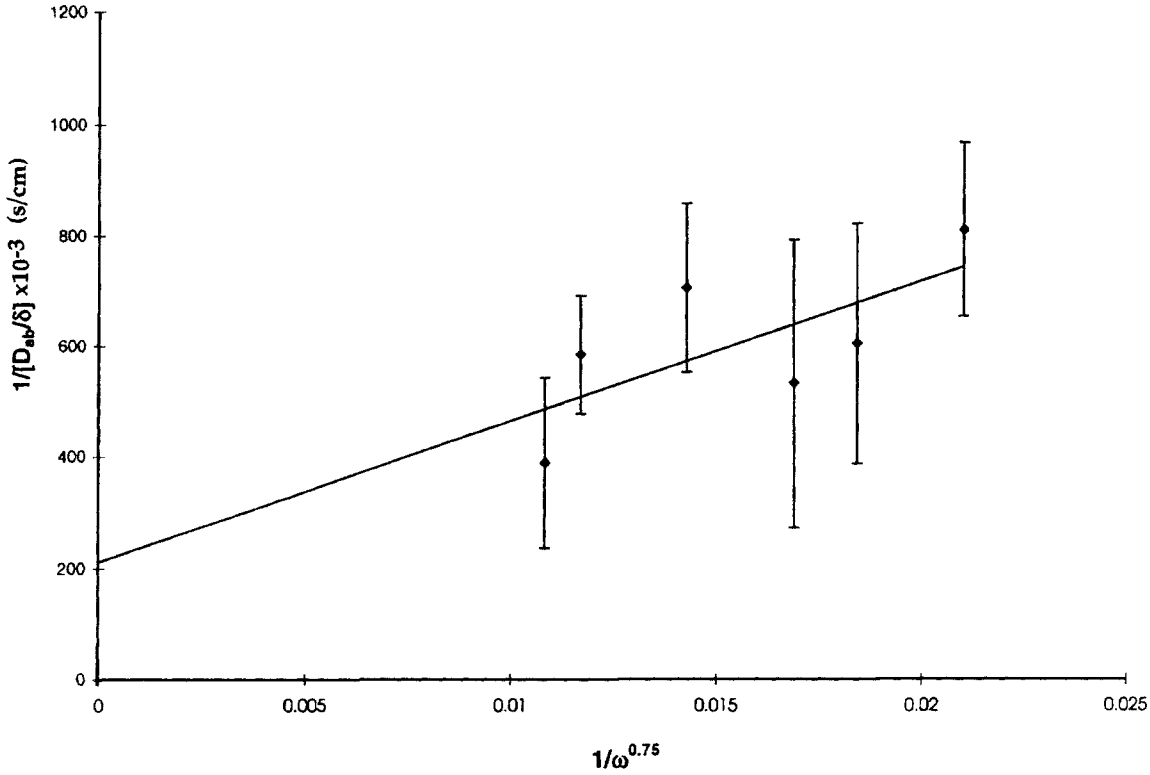

Figure 3. Determination of 1,2-DCA overall mass-transfer coefficient as a function of stir rate in the stirred diaphragm cell.

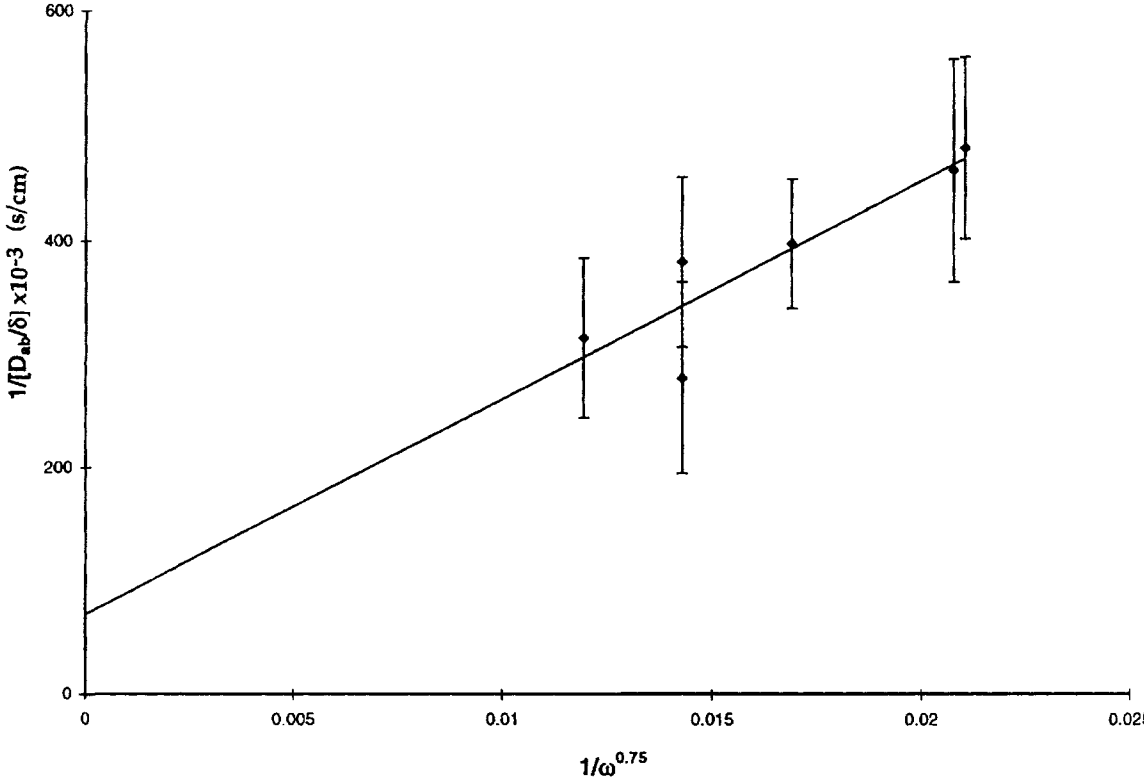

Figure 4. Determination of TCE overall mass-transfer coefficient as a function of stir rate in the stirred diaphragm cell.

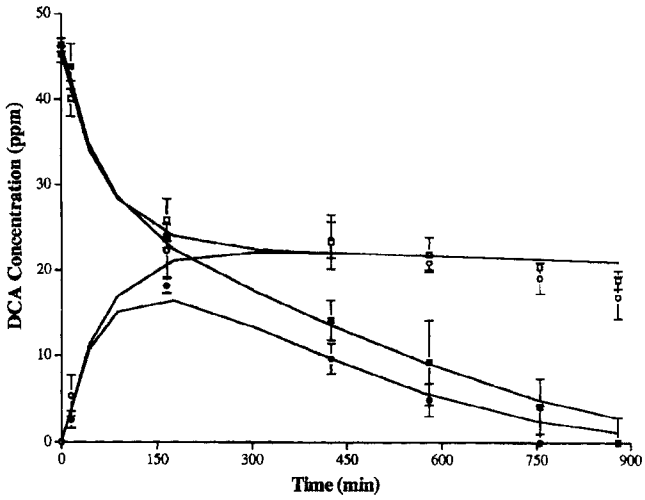

Figure 5. Biotic and abiotic batch diaphragm cell 1,2-DCA feed and permeate concentration with initial feed concentration of 46 ppm.

— Model; □ feed, abiotic; ○ permeate, abiotic; ■ feed, biotic; ● permeate, biotic.

Batch diaphragm cell experiments with 1,2-DCA

Experiments were conducted for an initial 1,2-DCA concentration of 46.4 ppm. The solute concentration in the permeate and feed chambers of both abiotic and reacting diaphragm cells was monitored at approximately 1-h intervals for at least 24 h. The changes in feed- and permeate-chamber solute concentrations in the diaphragm cells are plotted as a function of time and compared to the mathematical-model results (Figure 5). The error bars represent one standard deviation from the mean value of the replicate concentration measurements for all figures except Figures 6, 10, and 12, where they represent three standard deviations from the mean.

The initial and final protein concentrations in the biological medium were measured in the diaphragm cell experiments conducted with microorganisms. 1,2-DCA biodegradation showed a lag period of a least 1 h; thereafter the biodegradation rate was quite rapid until 1,2-DCA concentrations approached zero. In the abiotic experiment equilibrium conditions were established within 3 to 4 h. Thus, in order to evaluate the solute flux enhancement it was necessary to calculate the diffusive flux within the first 1 to 3 h of the experimental period. The magnitude of diffusive flux in the time period just indicated was calculated using Eq. 5 and was determined to be 1.35×10^{-6} mmol/cm^2/min for the abiotic system and 2.18×10^{-6} mmol/cm^2/min in the presence of *X. autotrophicus* GJ10 (Table 1). The flux enhancement ratio was determined to be 1.61, and the percent removal was approximately 100%.

The batch diaphragm cell experiment was repeated with a high initial 1,2-DCA concentration of 72.7 ppm. The solute concentration in the permeate and feed chambers of both abiotic and biological batch diaphragm cells was monitored at approximately 1-h intervals for at least 24 h. The changes in solute concentration in the upper and lower chambers with time are shown along with the concentrations predicted by the mass-balance model (Figure 6). The 1,2-DCA fluxes obtained in the abiotic and biological experiments were 3.7×10^{-7} mmol/cm^2/min and 9.63×10^{-7} mmol/cm^2/min, respectively (Table 1). The flux enhancement ratio was 2.6 and 100% removal of 1,2-DCA was obtained.

Table 1. Solute Flux in the Presence and Absence of Biological Reaction

Experiment No.	Flux (j) with Reaction (mmol/cm^2/min)	Flux (j) Abiotic (mmol/cm^2/min)
1. Batch diaphragm cell 46 ppm 1,2-DCA (165 min)	2.18×10^{-6}	1.35×10^{-6}
2. Batch diaphragm cell 72.7 ppm 1,2-DCA (270)	9.63×10^{-7}	3.7×10^{-7}
3. Batch diaphragm cell 3.6 ppm TCE (100 min)	4.31×10^{-7}	2.17×10^{-7}
4. Batch diaphragm cell 21.5 ppm TCE (100 min)	1.70×10^{-6}	1.31×10^{-6}
5. Membrane flow cell 35.6 ppm 1,2-DCA (steady state)	8.78×10^{-6}	5.61×10^{-6}
6. Membrane flow cell 7 ppm TCE (steady state)	9.2×10^{-7}	3.5×10^{-7}
7. Hollow-fiber bioreactor 1,2-DCA (steady state)	8.78×10^{-10}	1.84×10^{-9}

Batch diaphragm cell experiments with TCE

Batch diaphragm cell experiments were conducted for TCE feed concentrations of 3.6 and 21.5 ppm. In the biological-reaction experiments resting cells with no carbon source were used. The TCE concentrations in the permeate and feed chambers of both the abiotic and biological batch diaphragm cells were monitored at approximately 1-h intervals for at least 24 h. The change in TCE concentration with time in the upper and lower chambers is shown in Figure 7. Equilibrium conditions were established within 2 to 3 h in the abiotic experiment. Thus, in order to evaluate the flux enhancement ratio it was necessary to calculate the solute flux within the

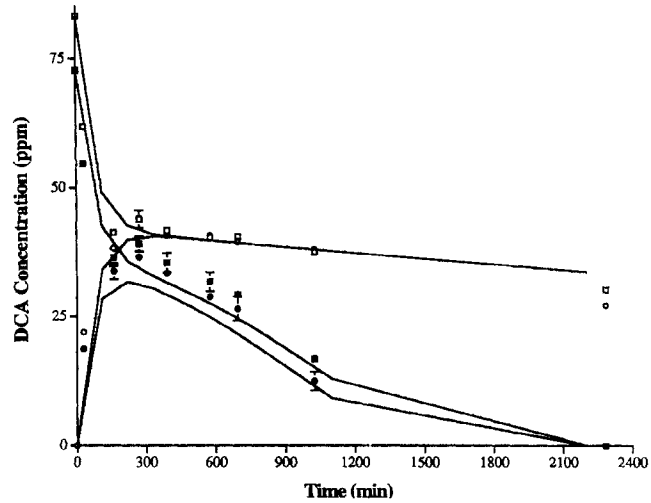

Figure 6. Biotic and abiotic batch diaphragm cell 1,2-DCA feed and permeate concentration with initial feed concentration of 72.7 ppm.

— Model; □ feed, abiotic; ○ permeate, abiotic; ■ feed, biotic; ● permeate, biotic.

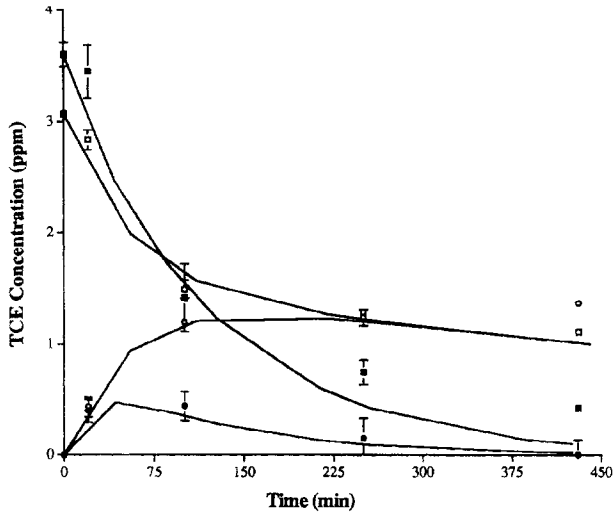

Figure 7. Biotic and abiotic batch diaphragm cell TCE feed and permeate concentration with initial feed concentration of 3.6 ppm.

— Model; □ feed, abiotic; ○ permeate, abiotic; ■ feed, biotic; ○ permeate, biotic.

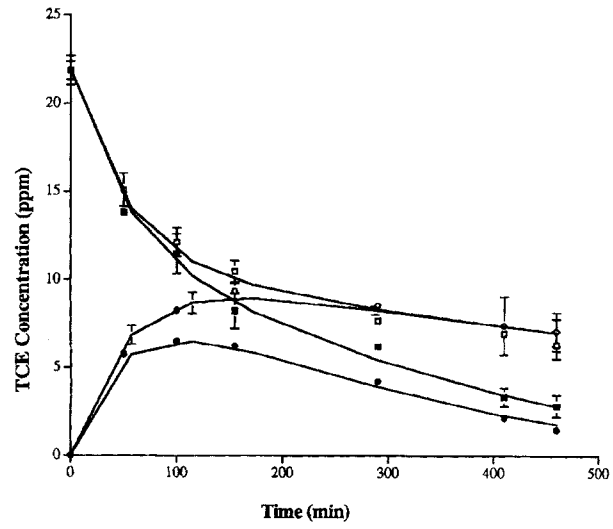

Figure 8. Biotic and abiotic batch diaphragm cell TCE feed and permeate concentration with initial feed concentration of 21.5 ppm.

— Model; □ feed, abiotic; ○ permeate, abiotic; ■ feed, biotic; ○ permeate, biotic.

experimental time period of 1 to 3 h. The magnitude of diffusive flux in the time period just indicated was determined to be 2.17×10^{-7} mmol/cm^2/min and 4.31×10^{-7} mmol/cm^2/min for the abiotic and biological systems, respectively. The flux enhancement ratio obtained experimentally was 2.0, and approximately 100% percent removal of TCE was obtained.

The batch diaphragm cell experiments were repeated with a high initial TCE concentration of 21.5 ppm. The solute concentrations in the permeate and feed chambers of both abiotic and biological reaction diaphragm cells were monitored at approximately 1-h intervals for at least 24 h. The changes in solute concentration in the upper and lower chambers with time are shown in Figure 8. Experimental data from both abiotic- and biological-reaction experiments were analyzed to evaluate the TCE solute flux (Table 1) and the flux enhancement ratio. The TCE flux in the abiotic experiment was 1.31×10^{-6} mmol/cm^2/min, while that in the presence of microorganisms was 1.7×10^{-6} mmol/cm^2/min, yielding a flux enhancement ratio of 1.30. Approximately 86% removal was achieved in the biological system. An overall material balance was made on the abiotic experiment data to determine the magnitude of solute losses. At high TCE concentration solute degradation showed a lag period of at least 1 h, and therefore was quite rapid until approximately 6 h, when no additional removal was observed. At the low concentration of 3.6 ppm TCE the solute was completely removed within the first 6 h.

Microbial enhancement of TCE and 1,2-DCA solute flux and removal efficiency in the flow diaphragm cell

The stirred flow-cell reactor was designed to study the biological enhancement of solute flux in a continuous-flow system, which unlike the batch experiments may be operated at steady state. Experiments were first conducted abiotically to determine the overall mass-transfer coefficient, solute flux in the absence of microorganisms, and to determine the significance of solute loss due to volatilization.

Continuous-flow diaphragm cell with 1,2-DCA

The abiotic control experiment for 1,2-DCA was conducted at an initial concentration of 35.6 ppm. The aqueous feed to the upper chamber containing the model compound was pumped at a rate of 1.1 mL/min, while the permeate feed was pumped at 1.5 mL/h. Samples from aqueous feed inlet, outlet, and permeate outlet were monitored every 30 to 40 min. A plot of the change in concentration of the feed inlet, outlet, and permeate outlet streams with time is shown in Figure 9.

The system approaches steady state in about 6 h. The experiment was repeated with microorganisms under identical conditions with a similar initial 1,2-DCA feed chamber concentration. The feed inlet, outlet, and permeate outlet concentrations were monitored at 40- to 60-min intervals. It is apparent from a plot of 1,2-DCA concentration that the system approaches steady state within 16 h (Figure 10).

Using the data from the abiotic-control and biological-reaction experiments, 1,2-DCA solute flux was calculated as 5.61×10^{-6} mmol/cm^2/min and 8.78×10^{-6} mmol/cm^2/min, respectively, using Eq. 5 (Table 1). Approximately 40% removal of 1,2-DCA was obtained in the biological system. The flux enhancement ratio was determined to be 1.57 from Eq. 6.

Continuous-flow diaphragm cell with TCE

Flow diaphragm cell experiments were conducted for TCE under similar flow conditions. The abiotic control experiment was conducted at an initial TCE concentration of 7 ppm. The feed inlet, outlet, and permeate streams were sampled every

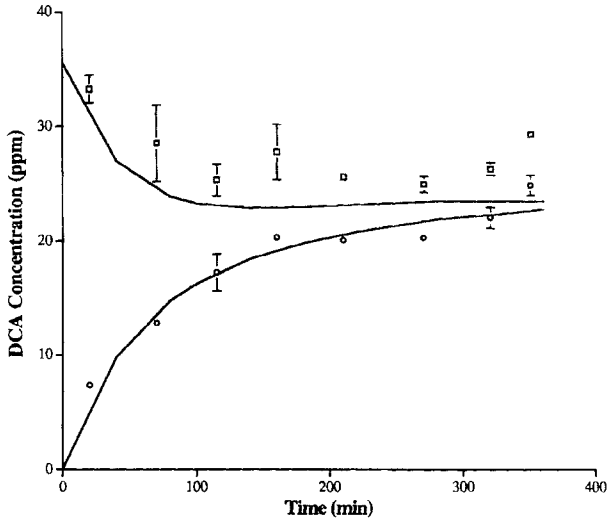

Figure 9. Feed and permeate 1,2-DCA concentrations in the abiotic membrane flow cell.

— Model; □ feed outlet, abiotic; ○ permeate outlet, abiotic.

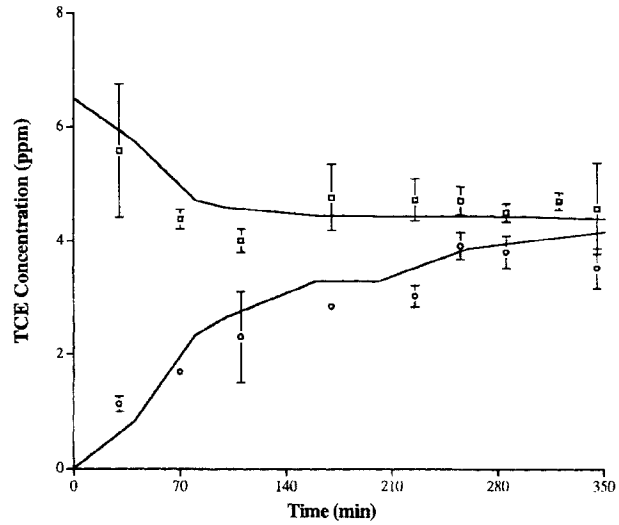

Figure 11. Feed and permeate TCE concentrations in abiotic membrane flow cell.

— Model; □ feed outlet; ○ permeate outlet.

40 to 60 min. It is apparent from the concentration vs. time data (Figure 11) that the system approaches steady state in approximately 6 h. Physical losses of TCE were calculated by an overall material balance at steady state as well as at each sampling time point.

The experiment was repeated under identical conditions with microorganisms. The change in concentration of the model compound in the inlet and outlet streams was monitored as a function of time. The data indicate that the system approaches steady state in approximately 300 min (Figure 12). Using the data from these experiments, the TCE solute flux in the presence of *P. cepecia* $PR1_{31}$ was determined to be 9.2×10^{-7} mmol/cm^2/min. Approximately 68% removal of TCE was obtained in the biological experiment. Data from the abiotic-control experiment were used to perform an overall material balance on the system and determine physical losses. The steady-state permeate-outlet and feed-outlet concentrations in the abiotic control experiment are in close agreement with the values predicted by the model.

In the biological experiment steady-state concentrations of TCE in the feed and the permeate streams are considerably higher than the values predicted by the model. This deviation can be expected since *P. cepecia* $PR1_{31}$ is in a resting stage with no carbon source. The batch diaphragm cell data that were conducted under these conditions showed a similar result where most of the TCE was removed within the first 6 h

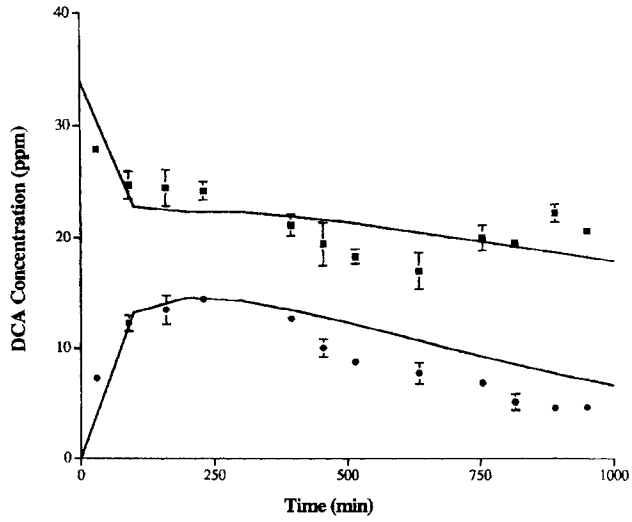

Figure 10. Feed and permeate 1,2-DCA concentrations in membrane flow cell with *X. autotrophicus* GJ10.

— Model; ■ feed outlet; ● permeate outlet.

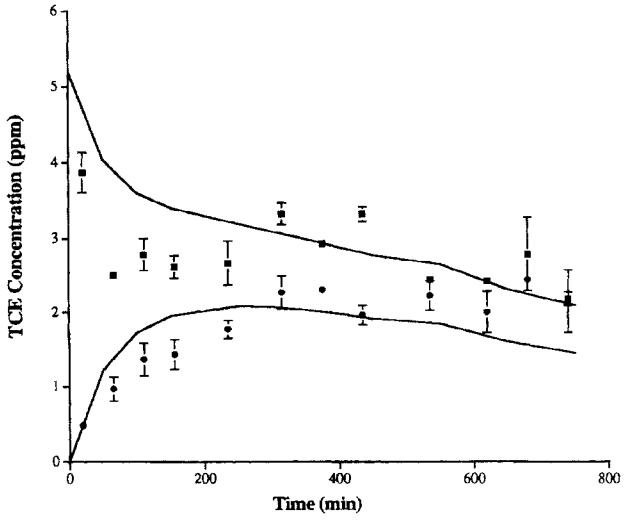

Figure 12. Feed and permeate TCE concentrations in membrane flow cell with *P. cepacia* $PR1_{31}$.

— Model; ■ feed outlet; ● permeate outlet.

of experimental time. The batch kinetic data repeat this phenomenon in that 70% of the TCE was removed within the first 6 to 8 h and no significant degradation was observed in the rest of the experiment. A careful examination of the concentration vs. time plot indicates this phenomenon to be occurring in the time range of 300 to 400 min. Hence, most of the removal has occurred within the first 6 h.

Since the biological-reaction experiment was conducted at a lower TCE concentration than the abiotic-control experiment, the solute flux in the absence of reaction was calculated using abiotic model results and was determined to be 3.5×10^{-7} mmol/cm^2/min (Table 1). The flow-cell reactor configuration yields a flux enhancement ratio of greater than 2.6, with a removal efficiency of 38%. However, this experiment would undoubtedly have yielded a higher flux enhancement ratio and removal efficiency if the biological reaction had not ceased.

Determination of the overall mass-transfer coefficient in the hollow-fiber membrane bioreactor

The abiotic-control experiment for 1,2-DCA was conducted at an average initial feed concentration of 36.86 ppm. Flow conditions were maintained as for the abiotic experiment. Feed inlet, outlet, and permeate outlet solute concentrations were monitored every 2 to 3 h. Using the steady-state inlet and outlet concentration, the overall mass-transfer coefficient was calculated from Eq. 15 to be 7.6×10^{-6} cm/min. This is lower than the value of 1.7×10^{-5} cm/min that was estimated for the system using various correlations (Yun et al., 1992; Yang et al., 1986; Zander et al., 1989). The system approached steady state in about 16 h and the 1,2-DCA solute flux was calculated to be 8.78×10^{-10} mmol/cm^2/min from Eq. 11.

Examination of flux enhancement and removal efficiency in a hollow-fiber membrane bioreactor

The experiment was repeated under identical flow conditions at an average initial 1,2-DCA feed concentration of 25.4 ppm with microorganisms. The feed inlet, outlet, and permeate outlet 1,2-DCA concentrations were monitored at 2–3-h intervals initially and at 6-h intervals after 40 h (Figure 13), and the 1,2-DCA flux was calculated (Table 1). All samplings were conducted in duplicate. Despite the high surface area per unit volume in the hollow-fiber reactor, the solute flux enhancement ratio obtained experimentally is only 0.78. However, the value predicted by the mathematical model was 1.24. The experimentally determined overall transfer coefficient in the hollow-fiber reactor was lower in the presence of growing microorganisms, which may reflect biofilm fouling of the membrane surface. The membrane was not microscopically examined for fouling or the formulation of biofilms; however, there was visible evidence of fouling.

Summary of results

A summary of the solute fluxes obtained in each of the experiments is given in Table 1. Excluding the hollow-fiber bioreactor results, the solute flux obtained in the presence of microbial degradation of solute was approximately 30 to 160% greater than that obtained in the absence of microbial reaction. The magnitude of the solute flux enhancement obtained would be even greater for biological reactions with significantly faster kinetics.

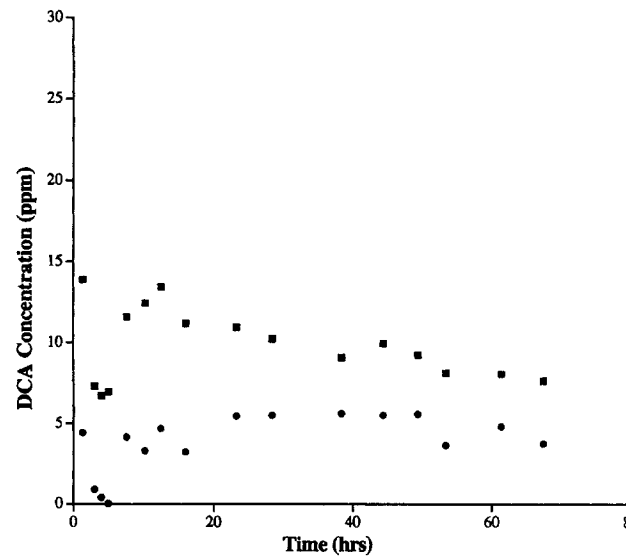

Figure 13. Feed and permeate 1,2-DCA concentrations in a hollow-fiber bioreactor with *X. autotrophicus* GJ10.

■ Feed outlet; ● feed inlet.

The magnitude of the solute flux enhancement obtained experimentally was compared to that predicted by the solute mass-balance models developed. The relative errors of experimentally determined variables, such as analytical determination of concentration and sampling and extraction techniques, where applicable, were used in the logarithmic differentiation error analysis of McCracken (1984) to determine the relative error associated with the calculation of the solute flux enhancement ratios (Inguva, 1996). Thus, the experimentally determined flux enhancement due to reaction in the diaphragm cell systems is accurately represented by the mathematical models developed for the diaphragm cell experimental systems. The solute flux enhancement predicted by the mathematical models for each experimental system is within one relative experimental error interval of those measured, excluding the hollow-fiber bioreactor determination (Figure 14).

Conclusions

Biological reactions can have a significant impact on solute mass-transfer fluxes in ultrafiltration membrane separation operations. Experimental data from both batch and flow stirred diaphragm cells indicate significant enhancement of solute flux in the presence of microbial reaction. The values obtained experimentally are consistent with those predicted by the mathematical model (Figure 14). The 1,2-DCA flux obtained in the stirred membrane flow cell with reaction is at least 1,000-fold higher than that obtained in a hollow-fiber reactor. This indicates that stirred membrane reactors are a good choice for examining flux enhancement due to microbial reactions. In the hollow-fiber reactor, 1,2-DCA was removed with an efficiency greater than 66%. Although the

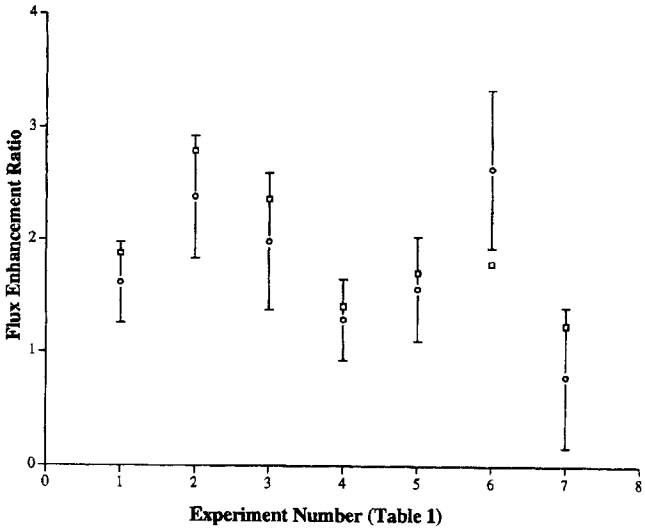

Figure 14. Comparison of experimentally obtained solute-flux enhancement to mathematical model prediction of solute-flux enhancement.

□ Predicted; ○ experimental.

surface area per unit volume is high in this configuration, the mass-transfer resistance is also high, with a much greater potential for biofilm fouling of the membrane. A reactor design possessing high surface area per unit volume, which also minimizes mass-transfer resistances, will allow for solute fluxes closer to those observed in the stirred diaphragm cells, and hence, improved UF membrane bioreactor performance.

The solute flux in the shell and tube hollow-fiber membrane bioreactor was determined to be 8.78×10^{-10} mmol/cm^2/min. Solute fluxes were calculated for a similar reactor configuration under identical flow conditions for solvent extraction and pervaporation processes for removal of chlorinated hydrocarbons. The solute flux obtained in a solvent extraction system was approximately 4.73×10^{-8} mmol/cm^2/min (Hutter et al., 1994). The solute flux obtained in a pervaporative system under identical conditions was 1.88×10^{-7} mmol/cm^2/min (Lipski and Cote, 1990). Although the magnitude of solute flux in the HBR is lower, the biological process may be preferable, since the contaminants are completely destroyed and not merely concentrated into another stream requiring subsequent destruction or disposal. Solute fluxes obtained in the stirred diaphragm cells with reaction ranged from 4.3×10^{-7} to 8.78×10^{-6} mmol/cm^2/min. Hence, solute fluxes obtained in the stirred flow-cell membrane reactors in the absence of large film resistances are comparable to, or greater than, those obtained in current solvent extraction and pervaporation operations.

The enhancement of solute flux by microbial reaction has important implications for the design and operation of membrane bioreactors in environmental as well as biotechnology applications. In many cases removal by biological reactions is slower than in separations driven by physical or chemical reactions; hence, process flow rates must be lower to achieve the desired separation and reaction. At low flow rates, however, the film resistance increases, resulting in decreased solute flux. Thus the solute flux and percent removal obtained reciprocate each other; hence, optimal reactor design is required to achieve maximum flux with good removal efficiencies. Further strategies that enhance solute partitioning in the permeate, such as micellar extraction or inclusion of a cosolvent in the permeate, may enhance solute partitioning in the permeate and reduce the permeate side film resistance in addition to increasing the solute concentration in the permeate, resulting in increased biodegradation rates. The effect of such strategies on the solute flux, biodegradation rate, and the overall removal may be easily examined in a stirred flow-cell reactor.

These studies demonstrate that a UF membrane-based biodegradation process is feasible for removal and destruction of chlorinated aliphatic hydrocarbons from dilute aqueous streams. The experimental methodology outlined allows us to determine the solute flux and removal performance obtainable in the absence of significant film resistances typical of most shell and tube HBR configurations. Knowledge of the maximum achievable solute flux and the effect of microbial enhancement of solute flux may be useful in the design and operation of more complex membrane reactor configurations.

Notation

A = membrane contact area (L^2)
C_{f_0}, C_{p_0} = inlet concentrations of solute on feed and permeate sides (M/L^3)
C_{f_e}, C_{p_e} = exit concentration of solute on feed and permeate side (M/L^3)
d = length of stir bar (L)
d_{it} = tube diameter (L)
D = diffusion coefficient of solute in membrane (L^2/T)
j = diffusive flux ($mol/L^2 \cdot T$)
k = maximum specific degradation rate (M/MT)
K_0 = overall mass-transfer coefficient (L/T)
k_f = mass-transfer film coefficient (L/T)
K_s = half saturation constant (M/L^3)
Q_f = volumetric flow rate of the feed (L^3/T)
Q_p = volumetric flow rate of the biomedium (L^3/T)
t = time (T)
V_t = volume of the feed in top compartment in the diaphragm cell (L^3)
V_b = volume of the biomedium in bottom compartment in the diaphragm cell (L^3)
V = culture volume (L^3)
X = cell density (M/L^3)

Greek letters

ρ = density of water (M/L^3)
μ = specific growth rate of the microorganism (1/T)
v = kinematic viscosity (L^2/T)
δ = membrane thickness (L)
ω = stir-bar revolutions per time

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