Membrane-based gas transfer: an environmental engineering laboratory

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Abstract We propose an educational experience in which students design a membrane gas transfer reactor, construct a bench-scale version in the laboratory, and employ the reactor to measure mass transfer coefficients. The membrane reactor is useful for teaching mass transfer principles because the mass transfer interface is well defined and easily observed. The system can be modeled successfully using straightforward mathematics. The reactor can be designed and constructed by students, using the mathematical model as a basis, providing insight into the physical meaning of model parameters. The proposed membrane system can be readily operated to obtain data that can be employed to develop or modify existing mass transfer correlations. This can provide students with significant insight into the development of mass transfer correlations and how the constants in such correlations are typically determined. These features help promote a deeper understanding of mass transfer principles.

Keywords Laboratory experience; membrane gas transfer; process design

Introduction
It has been the author’s experience that students find the process of mathematically modeling physical systems quite challenging. One possible reason is that students seem to have few opportunities to apply the concepts learned in calculus to systems that are real, but simple enough to allow successful application of undergraduate-level mathematics. A second reason stems from the fact that students often have difficulty visualizing the system being modeled. This difficulty is exacerbated when the rate of mass input or output involves mass transfer. In mass transfer applications, it is necessary to visualize the geometry of the interface across which mass diffuses. The geometry may be complex (e.g., DNAPL ganglia) and/or it may be a simplified abstraction of a real interface – for example, the complex surface of a lake, with waves and undulations, may be modeled as a planar surface. Finally, students may have difficulty building mathematical models when they find the physical meaning of parameters contained in such models too abstract.

The membrane reactor has unique advantages from the point of view of improving students’ ability to visualize mass transfer processes, and could be justified on that basis alone. In addition, the use of such reactors is increasing in many areas of environmental engineering, including water and wastewater treatment, and hazardous waste site remediation. As a result, it has become important to incorporate membrane processes into the environmental engineering curriculum. One approach taken in our curriculum is to introduce membrane processes as an extension of gas transfer, an important class of membrane process applications. Membrane gas transfer may include bubbleless transfer of oxygen or air in wastewater treatment (Côté, 1989), volatile organic compound stripping (Semmens et al., 1989), transfer of hydrogen in site bioremediation applications (Haugen et al., 2002; Fang et al., 2002), and transfer of ozone in potable water disinfection.

Gas transfer is a fundamental topic in the environmental engineering curriculum. In the Rensselaer curriculum, various thermodynamic and mass transfer aspects of this topic are addressed in the introduction to environmental engineering, biological processes, physico-
chemical processes, mass transfer processes and chemodynamics courses. Gas transfer is an excellent vehicle for demonstrating basic principles of vapor–liquid equilibrium and mass balance. In more advanced treatments, gas transfer can be used as a means to introduce mass transfer theories, including film theory. In this context, the analogy of a real film (membrane) and a hypothetical film at the air–water interface can be exploited. Finally, gas transfer provides a useful framework for developing ideas about dimensional analysis and mass transfer correlations. In this paper, we describe the design, construction, testing, and analysis of a membrane gas transfer module suitable for use in one or more environmental engineering laboratory courses, or as a demonstration unit in a lecture course. It is feasible to have student groups each construct their own module for testing and analysis, providing an opportunity to emphasize design and fabrication.

The membrane reactor is useful for teaching mass transfer principles because the mass transfer interface is well defined and easily observed. The system can be modeled successfully using straightforward mathematics. The reactor can be designed and constructed by students, using the mathematical model as a basis, providing insight into the physical meaning of model parameters. The proposed membrane system can be readily operated to obtain data that can be employed to develop or modify existing mass transfer correlations. At the undergraduate level, concepts such as Henry’s law, simple mass transfer, reactor modeling, and dissolved gas measurement could be emphasized. In a more advanced course, the emphasis might be placed on mass transfer theory, developing shell balances and mass transfer correlations.

**Process design**

A one-semester design course titled “Bench scale design” was offered as a prototype to gain experience with the proposed membrane system. The course was offered to graduate students; however, based on our experience, we feel it would be suitable as an undergraduate course. Students were challenged to design, build and test (characterize) a membrane-based oxygenation process. It was specified that process characterization must include measurement and correlation of the overall mass transfer coefficient. Therefore, implicit in the design statement was the need to have inlet and outlet oxygen concentrations that could be readily measured in the laboratory; this could be viewed as a design constraint. A hollow fiber membrane configuration was suggested, and guidance was provided regarding the choice of mass transfer correlation to use in the design, and the development of the design equations. A schematic of the design procedure is shown in Figure 1.

All design parameters used in the mass transfer correlation and the design equation are employed directly or indirectly in building and/or operating the process. Students reported that this promoted a deeper understanding of the mathematical terms that appear in the models, allowing them to take on more physical meaning. For example, students have the opportunity to “see” how values of Reynolds number manifest in terms of a constructed system. The design basis contains many degrees of freedom, which emphasizes to students the fact that there are many possible solutions to a design problem. All design choices bear on the desired outcome of the process, which is to obtain oxygenated water from an oxygen-free feed. Therefore, it was necessary to develop a design model to facilitate the analysis of design options.

**Reactor model**

Assuming steady-state plug flow conditions, and neglecting the effects of dispersion in the liquid phase, the differential balance of oxygen in the shell-side aqueous phase is:

\[
0 = -u_L \frac{dC_L}{dx} + K_L \left(C_{L,SAT} - C_L\right)\]  

(1)
where \( C_L \) is the aqueous phase oxygen concentration, \( u_L \) is the liquid phase interstitial velocity [m/s], \( a \) is the specific membrane surface area \([m^2/m^3]\), \( x \) is the axial distance from the inlet, \( K_T \) is the overall mass transfer coefficient based on a liquid phase gradient [m/s], and \( a \) is the specific surface area for mass transfer \([m^2/m^3]\). The \( C_{L,SAT} \) term, which is the aqueous phase oxygen concentration corresponding to an equilibrium condition with the gas phase oxygen concentration, is a challenging idea for students to grasp (especially at the undergraduate level). One approach is to describe the \((C_L - C_{L,SAT})\) term as a departure from equilibrium, which is the driving force for mass transfer. In this system, as in air strippers or gas absorber columns, \( C_{L,SAT} \) varies along the length of the fiber, because the oxygen partial pressure in the membrane must vary from the feed pressure to atmospheric pressure at the outlet. One approach is to express \( C_{L,SAT} \) in terms of \( C_L \) using an overall mass balance around the control volume shown in Figure 2:

\[
C_{L,SAT} = \frac{C_G}{H} = \frac{Q_L C_{L,IN}}{Q_G} + \frac{C_{G,IN}}{H} - \frac{Q_L C_L}{Q_G H}
\]

(2)

In writing Eq. (2), we assume that the gas flow rate is high enough to assure negligible loss of oxygen along the fiber, which means that the gas flow rate, \( Q_G \), can be treated as constant. In developing the design model, students felt they gained an understanding of the importance of “selecting appropriate assumptions” and the consequence of making assumptions. Substituting Eq. (2) into Eq. (1) and integrating with the boundary condition \( C_L = C_{L,IN} \) at \( x = 0 \) yields the design equation:
The gas and liquid flow rates \( Q_G \) and \( Q_L \), the gas and liquid inlet concentrations \( C_{G,IN} \) and \( C_{L,IN} \) are selected, and Henry’s constant, \( H \), is known as a function of temperature. The specific surface area, \( a \), is computed from the fiber properties (size and number) selected. To use the design equation, an estimate of the overall mass transfer coefficient \( K_L \), must be made. Several correlations are available in the literature; one example is the correlation proposed by Costello et al. (1993):

\[
\frac{k d_h}{D} = \alpha \left[ \frac{u d_h}{v} \right]^{0.53} \left[ \frac{v}{D} \right]^{0.33}
\]

(4)

where \( k \) is the mass transfer coefficient, \( D \) is the oxygen diffusion coefficient in water, and \( \alpha \) is a constant related to the volume fraction of the membrane within the shell (packing density). Costello et al. (1993) recommend \( \alpha = 0.53 - 0.58 \phi \), where \( \phi \) is the volume fraction of the membrane. The Sherwood and Reynolds numbers are calculated using the interstitial velocity and the hydraulic diameter, \( d_h \), based on the shell cross-section; \( d_h = 4A_{flow}/W_p \) where \( W_p \), the wetted perimeter, is equal to the total fiber circumference. Measurements of \( C_L \) made using the completed module are later used to obtain measured values of \( K_L \), which are then used to calibrate the mass transfer correlation used during design.

**Module prototype**

The following describes in some detail a successful prototype design. This design can be used as a model to provide guidance to students when they are presented with a full design/build problem, or used as a template for constructing modules for use in single-session laboratory experiences.

**Membrane materials.** Dense (non-porous) polydimethylsiloxane (PDMS, silicone rubber) was chosen for this design because it offers good oxygen transfer properties, is readily available, and is relatively inexpensive. Silastic platinum-cured silicone tubing was obtained from Dow Corning, Midland, Michigan. Dense membranes can be operated at higher pressures without forming bubbles, but present a higher resistance to mass transfer than their microporous counterparts (Ahmed and Semmens, 1992). The membranes employed have an internal diameter of \( 0.30 \pm 0.10 \) mm, outside diameter \( 0.64 \) mm and wall thickness of \( 0.15 \pm 0.10 \) mm. A total of 24 fibers were potted into the module with effective working length of 150 cm and total surface area of 724 cm\(^2\).

**Module manufacture.** The module shell was constructed from \( \frac{3}{4} \)-inch transparent PVC, with a length of 156 cm. The module was designed for gas flow in the membrane lumen and water flow in the shell annulus. While some manufacturers weave fibers into a fabric to obtain more uniform spacing, or add baffles to induce flow normal to fiber surfaces, flow parallel to the fibers was chosen for simplicity. Fibers were gathered in a bundle and “potted” into the shell using epoxy (Figure 1). First, holes with female NPT pipe threads were made along the pipe for the water inlet, outlet, and sampling ports. Holes for the water inlet and outlet were made 3 cm from each pipe end to allow 2 cm for epoxy and pipe-to-tube adaptors. These holes would also serve as filling port for the epoxy during potting. Then, silicone rubber membranes, obtained from the manufacturer in rolls, were cut to 170 cm lengths. A bundle of 24 such fibers was routed through the shell. Fibers were supported
temporarily by routing the ends through small holes pierced through a small piece of cardboard using a size-22 syringe needle, which is the size of membrane outside diameter (Figure 3). Plumbing glue was then used to temporarily fix the cardboard to end of the shell. The assembly was then supported vertically, and potting epoxy (3M™ Scotch-Weld™ Epoxy Potting Compound DP270) was poured through the port nearest the bottom end of the shell to a depth of 2 cm.

After the epoxy hardened, the pipe was turned upside down and the potting procedure was repeated. After the epoxy cured completely, a utility knife was used to separate the cardboard from the shell, exposing the fiber openings at both ends of pipe. The module was finished by solvent welding an adapter (¾-inch PVC socket to ½-inch pipe) over the shell end. A reducing bushing (¾-inch to ½-inch PVC) was threaded into the adapter to accommodate a barbed hose end adapter (½-inch pipe to ¼-inch barbed hose end), which was then connected to ¼-inch laboratory-grade PVC tubing.

**Experimental setup.** A schematic depiction of the membrane system is shown in Figure 4. Feed water was pumped to the water inlet on one side of the membrane module from a 6-L plastic tank using a peristaltic pump (MasterFlex® Cole-Parmer Instrument Company, IL) with either 16 or 17 size tubing at flow rates in the range 0.27–4.52 mL/min. Feed water was deoxygenated by adding 60-mg/L sodium sulfite and 0.2-mg/L cobalt chloride, and mixed completely for several minutes until the dissolved oxygen concentration stabilized at a concentration near zero. Water was pumped from the feed reservoir into the module shell and the flow rate was measured using a graduated cylinder and a stopwatch. The resulting velocities through the membrane module were in the range 0.8–1.9 cm/s. All experiments were performed at room temperature (20–22°C).

Pure oxygen (industrial grade) was supplied from a gas cylinder connected to the gas inlet; pressures ranged from 100 to 275 kPa (15–40 psi). A two-stage regulator controlled the gas inlet pressure. Gas flow rate was verified using a bubble flow meter. As with commercial systems, the proposed membrane module can be used in either a flow-through or dead-end mode; the outlet gas valve is used for switching between modes. In the flow-through mode, oxygen is continuously fed through the fibers, and gas is vented to keep the partial pressure of oxygen high along the entire reactor length. In the dead-end mode, the gas outlet is sealed while the membrane is pressurized (Ahmed and Semmens, 1992). Experimental data reported here were collected in the flow-through mode. Dissolved oxygen concentrating in the module outlet was measured using a YSI Model 55 DO meter (Yellow Springs Incorporated, Ohio).

The DO probe has a measurement range of 0–20 mg/L, an accuracy of ±0.3 mg/L, and a
resolution of 0.01 mg/L. Calibration was done using a water-saturated sponge mounted in a built-in chamber. When the dissolved oxygen concentration reached steady state, the time was recorded and at least five readings of DO were taken. All flow-through tests showed that two to three hydraulic residence times were required to reach steady state.

**Mass Transfer Coefficient.**

Experimental conditions were varied to test a range of oxygen pressures and water velocities. The average overall mass transfer coefficients were calculated from water inlet and outlet dissolved oxygen concentrations, using the following form of Eq. (3):

\[
\ln\left(\frac{-\left[\frac{Q_L}{Q_GH} + 1\right]C_L + \frac{Q_L C_{L,IN}}{Q_GH} + \frac{C_{G,IN}}{H}}{C_{G,IN} - C_{L,IN}}\right) = -\frac{K_L a}{u_L} \left[\frac{Q_L}{Q_GH} + 1\right] x
\]

The mass transfer coefficient, \(K_L\), can be estimated from measurements of \(C_L\) as a function of \(x\); a plot of the logarithmic quantity on the left hand side of Eq. (5) versus \(x\) yields a slope proportional to \(K_L\). It was difficult to obtain data for the dissolved oxygen concentration as a function of position in the reactor using the YSI DO meter because a large sample size was required and sampling disturbed the flow and concentration profile significantly. Therefore, a single measurement of \(C_L\) at the outlet \((x = L)\) was employed. It is recommended that micro DO meters or in-situ probes be used to obtain the dissolved oxygen profile.

**Mass Transfer Correlation.** The mass transfer coefficients calculated from all runs ranged from \(2.6 \times 10^{-5}\) to \(1.1 \times 10^{-4}\) cm/s. The effect of velocity on mass transfer is shown in Figure 5. The data, expressed in terms of the Sherwood \((N_{Sh} = K_L d_L/D_L)\) and Reynolds \((N_{Re} = u d_L/\nu)\) numbers, were correlated as \(N_{Sh} = 1.07[N_{Re}]^{0.361}\). This data set corresponds to an inlet pressure of 208 kPa. The liquid phase diffusivity, \(D_L\), for oxygen was taken as \(2.1 \times 10^{-5}\) cm²/s. Incorporating the Schmidt number, the data in Figure 5 are described by the correlation \(N_{Sh} = 0.14[N_{Re}]^{0.361}[N_{Sc}]^{0.33}\), where the exponent on the Schmidt number \((N_{Sc} = \nu/D_L = 476)\) was taken as 0.33 for laminar flow conditions.

Students indicated that the process of fitting mass transfer data as shown in Figure 5 provided significant insight into the development of mass transfer correlations and how the constants in such correlations are typically determined.

**Effect of Gas Pressure.** The effect of gas pressure on the mass transfer coefficients was insignificant except for the runs made using the highest (4.52 ml/s) flow rates, in which case the mass transfer coefficients decreased somewhat at the highest pressures.
(240–275 kPa). This trend was found by Côté (1989) who suggested that the apparent decrease in performance at higher pressure could be related to the formation of micro-bubbles on the surface of the fibers.

**Comparison of liquid film and membrane resistances.** The total resistance was calculated from the overall mass transfer coefficient, and the membrane resistance was calculated from $\delta_e/(PH)$ using the following values: $\delta_e = 242 \times 10^{-6}$ m, $P$ (permeability of silicone rubber to oxygen) = $1.63 \times 10^{-13}$ mol/(m s Pa) and $H = 73,800$ Pa m$^3$/mol (Côté, 1989). The liquid film resistance was obtained by difference. Data generated here, shown in Figure 6, suggest that the membrane contributed no more than 3% to the total resistance. The dominant effect of liquid film resistance found here may be in part related to the low Reynolds numbers employed. The liquid film resistance was sensitive to hydraulic conditions, decreasing by about a factor of 3 over the $N_{Re}$ values employed.

**Conclusions**
In this paper, we described the design, construction, testing, and analysis of a membrane gas transfer module suitable for use in one or more environmental engineering laboratory courses. The proposed laboratory experience presents teaching opportunities in the areas of
phase equilibrium, mass transfer, reactor theory, and design. Construction of such a device is straightforward, and it should be possible for both undergraduate and graduate students to obtain good quality data. The system can be modeled successfully using straightforward mathematics.

The reactor can be designed and constructed by students, using the mathematical model as a basis, providing insight into the physical meaning of model parameters. The system helps students to visualize the geometry of the interface across which mass diffuses; in combination these features help promote a deeper understanding of mass transfer principles.

References