Correlation of Permeability and Solute Uptake in Membranes of Arbitrary Pore Morphology

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Membrane fouling is a phenomenon that plagues practically all ultrafiltration processes, and involves a buildup of solute (such as protein) molecules or particles on the external and internal pore surface of the asymmetric membrane. As a result, the effective pore size and porosity of the membrane decrease, with a concomitant decline in the solvent flux and an alteration of the sieving coefficient. There have been a number of attempts, generally based on the assumption of straight cylindrical pores, to qualitatively correlate the solute uptake with the decline in permeability (Fane et al., 1983; Matthiasson, 1983; Robertson and Zydney, 1990; Rodgers and Sparks, 1991; Kim et al., 1992; Brites and de Pinho, 1993). The reduction in permeability is attributed to a change in the cylindrical pore radius due to adsorption or deposition. Thus, if the calculated radial change is on the order of size of solute particle radius, it is usually assumed that a monolayer of solute has adsorbed in the membrane pores. However, this model frequently provides changes in pore radius substantially smaller than the solute molecular or particle radius. In these cases, it is assumed that less than a monolayer is adsorbed in the membrane pores, but no quantitative value for how much solute is adsorbed can be obtained. Further, it is well-known that the porous structure of most ultrafiltration membranes is of a complex geometry not well represented by parallel cylindrical pores. Thus, the model clearly lacks physical plausibility. It is, therefore, useful to develop a physically more appealing model that provides a quantitative correlation between adsorbed solute surface coverage and hydraulic permeability. This work develops such a model without recourse to a specific pore geometry, but rather in terms of independently measurable quantities: pore surface area and volume. Theoretical results are compared with previously published experimental results for protein uptake and hydraulic permeabilities (Robertson and Zydney, 1990) in ultrafiltration membranes.

Theory

The Kozeny-Carman equation (Kozeny, 1927), or equivalently, the d'Arcy equation (Jackson, 1977), is a commonly used model for describing flow through a packed-bed or a porous medium, and is generally accurate to within ±50% for flow vs. pressure drop predictions (Macdonald et al., 1979). For a porous medium comprised of arbitrary shaped and tortuous pores of varying cross section, it may be written in terms of hydraulic radius R_h, a concept that is very useful for nondescript geometry. Then, the hydraulic, or d'Arcy, permeability is

$$L_p = \frac{\epsilon}{\tau}\frac{R_h^2}{2L} \tag{1}$$

where ϵ is the void fraction, or porosity, of the membrane, L is the effective membrane thickness, and τ is the tortuosity factor. The hydraulic radius is defined as the ratio of the void volume available for flow and the wetted pore surface, and may be written as

$$R_h = \frac{V_p \epsilon}{(1-\epsilon)S_p}. \tag{2}$$

where V_p is the volume of the solid matrix and S_p is the wetted surface of the pores.

It is assumed here that Eq. 1 is valid for both a fouled and a clean membrane, albeit with different structural parameters. For a clean membrane, thus, Eq. 1 becomes

$$L_{p,o} = \frac{\epsilon_o}{\tau_o}\frac{R_{h,o}^2}{2L} \tag{3}$$

where the hydraulic radius for the clean membrane is also obtained from Eq. 2, but in terms of $V_{p,o}$ and $S_{p,o}$, the vol-

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ume of solid matrix and wetted pore surface area, respectively, for a clean membrane. When Eq. 2 is used for a fouled membrane, V_p and S_p refer to the effective structure that now includes the solid matrix of the membrane and the adsorbed solute. The tortuosity factor τ_o has typical values between 2 and 3. For instance, use of $\tau_o = 2.08$ in Eq. 3 yields the usual form of Kozeny-Carman equation (Bird et al., 1960), whereas the more recent study of Macdonald et al. (1979) recommends $\tau_o = 2.5$.

From Eqs. 1 and 3, the ratio of permeabilities of a fouled and a clean membrane is

$$\frac{L_p}{L_{p,o}} = \left(\frac{\tau_o}{\tau}\right)\left(\frac{\epsilon}{\epsilon_o}\right)\left(\frac{R_h}{R_{h,o}}\right)^2. \tag{4}$$

The void fraction is defined as:

$$\epsilon \equiv \frac{V_m - V_p}{V_m} = 1 - \frac{V_p}{V_m} \tag{5}$$

where V_m is the total volume of the membrane, that is, $V_m = AL$, and is assumed constant. An expression similar to Eq. 5 can be written for ϵ_o, and, thus, the ratio $V_p/V_{p,o}$ becomes

$$\frac{V_p}{V_{p,o}} = \left(\frac{1-\epsilon}{1-\epsilon_o}\right). \tag{6}$$

From Eqs. 2 and 6, the ratio of hydraulic radii of fouled and clean membranes becomes

$$\frac{R_h}{R_{h,o}} = \left(\frac{\epsilon}{\epsilon_o}\right)\left(\frac{S_{p,o}}{S_p}\right). \tag{7}$$

The use of Eq. 7 in Eq. 4 results in:

$$\frac{L_p}{L_{p,o}} = \left(\frac{\tau}{\tau_o}\right)\left(\frac{\epsilon}{\epsilon_o}\right)^3\left(\frac{S_{p,o}}{S_p}\right)^2. \tag{8}$$

Further, if we invoke the random pore model (Wakao and Smith, 1962; Datta and Rinker, 1985) that gives the tortuosity factor as inverse of the porosity, then

$$\frac{L_p}{L_{p,o}} \approx \left(\frac{\epsilon}{\epsilon_o}\right)^4\left(\frac{S_{p,o}}{S_p}\right)^2. \tag{9}$$

It now remains only to correlate the physical pore structure change of the membrane due to the fouling process. Figure 1 shows the envisioned physical model. Thus,

$$V_p = V_{p,o} + n_s V_s \tag{10}$$

where n_s is the number of solute particles adsorbed and V_s is the volume of each solute particle. More precisely, the second term on the righthand side of Eq. 10 should be multiplied by a packing factor β to account for any interparticle space made inaccessible to the flowing liquid due to close or multilayer packing. At low surface coverage of solute, of course, the particles are not in contact, and $\beta = 1$, while for close-packed or multilayer coverage, β is somewhat greater than unity. At any rate, using Eq. 5 in Eq. 10 yields

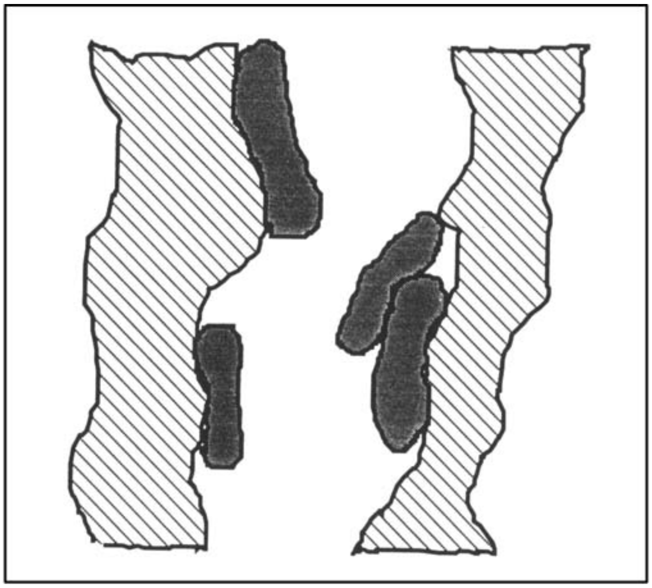

Figure 1. Pore cross section with adsorbed solute particles.

$$\frac{\epsilon}{\epsilon_o} = 1 - q_s \tag{11}$$

where

$$q_s \equiv \frac{n_s V_s}{V_m \epsilon_o} \tag{12}$$

and is the fraction of the membrane void volume occupied by the adsorbed solute particles. The fraction q_s may alternately be written in terms of the mass of the solute particles by using $n_s V_s = n_s(m_s/\rho_s) = M_s/\rho_s$ in Eq. 12. Thus, $q_s = M_s/\rho_s V_m \epsilon_o$, where m_s and ρ_s are the solute particle mass and density, respectively, and M_s is the total mass of adsorbed solute. Further, defining the mass of adsorbed solute per unit initial pore surface area, $M_s^* \equiv M_s/S_{p,o}$, we obtain

$$q_s = \frac{M_s^* a_m}{\rho_s} \tag{13}$$

where the specific membrane surface area of the unfouled membrane $a_m \equiv S_{p,o}/V_m \epsilon_o$.

Next, the overall wetted surface area for the fouled membrane is written as

$$S_p = S_{p,o} + n_s(1 - 2\gamma) S_s \tag{14}$$

where S_s is the surface area of each solute particle. The parameter γ is defined as the fraction of the solute molecule surface area that is not wetted by the flowing fluid due to adsorption or other surface contact. This is dependent upon the shape and rigidity of the solute particle, the pore geometry and rigidity, as well as the amount of solute adsorbed. γ is the only adjustable parameter in the model, with typical values ranging from zero to 0.5 for monolayer or lower coverage. For hard spherical solutes particles adsorbed on a hard pore surface γ will have a value approaching zero, while pliable and strongly adsorbed species could have γ values near 0.5. For closely-packed, or multilayer, adsorption, γ could be higher.

We may alternately write the surface area of each solute particle $S_s = a_s V_s$ where a_s is the specific surface of the solute particle. Then Eq. 14 may be written in the form

$$\frac{S_p}{S_{p,o}} = 1 + \frac{a_s n_s (1-2\gamma) V_s}{S_{p,o}} \tag{15}$$

Employing Eq. 12 and the definition of a_m in Eq. 15 yields

$$\frac{S_p}{S_{p,o}} = 1 + \alpha q_s \tag{16}$$

where the shape dependent parameter α is defined as

$$\alpha \equiv \frac{a_s}{a_m}(1-2\gamma). \tag{17}$$

It may be noted that α is negative for $\gamma > 0.5$.

Now, upon using Eqs. 11 and 16 in Eq. 8 then

$$\frac{L_p}{L_{p,o}} = \left(\frac{\tau_o}{\tau}\right)\frac{(1-q_s)^3}{(1+\alpha q_s)^2}. \tag{18}$$

Alternately, if the random pore model is assumed, from Eq. 9

$$\frac{L_p}{L_{p,o}} \approx \frac{(1-q_s)^4}{(1+\alpha q_s)^2}. \tag{19}$$

In summary, Eq. 18 correlates the hydraulic permeability of a fouled membrane to that of its initial clean state, the amount of the foulant adsorbed on its pore walls, and the shape dependent parameter α, defined by Eq. 17, involving independently measurable physical characteristics of the solute particles and the membrane pore geometry. The amount of solute adsorbed is given in terms of q_s, as defined by Eqs. 12 or 13. In addition, Eq. 18 involves change of the tortuosity factor due to fouling. If the random pore model is utilized for this purpose, Eq. 18 reduces to the simpler form given by Eq. 19. Alternately, this ratio may be assumed to be approximately unity.

The results can be used to either predict the decline in the hydraulic permeability as a function of the amount of a given solute adsorbed in the pores, or conversely, these expressions may be used to determine the number and total mass of the adsorbed solute particles from the hydraulic permeability data. If an independently determined value for the membrane pore surface area is not available, for instance by using the BET method, the hydraulic permeability data for a clean membrane could also be used to determine $S_{p,o}$ with the use of Eqs. 2 and 3, along with a knowledge of the initial void fraction and the total membrane volume. Conceptually, this model is more appealing and provides a better representation of the physics of the void loss due to solute adsorption than the commonly used cylindrical pore assumption. In addition, it is not necessary to assume any relationship between the adsorbed surface and the radial difference for the adsorbed species. It may also be noted that for the realistic case where γ can be assumed to be 0.5, α becomes zero and no information on species surface area is required in calculations involving Eq. 19.

Results and Discussion

To test the validity of this model, the experimental results of Robertson and Zydney (1990) were used. This is the most careful study, to date, for bovine serum albumin (BSA) adsorption on polyethersulfone membranes and its effect on hydraulic permeability. The reader is referred to the reference for details of the study, but, basically, initial and post-adsorbed hydraulic permeabilities for the thin skin of the asymmetric polyethersulfone membranes were determined for four different membranes, with molecular weight cutoffs (MWCO) of 50, 100 and 300 K, and 1 M. The solute uptake in the thin skin was also determined separately using radiolabeled BSA. For all membrane used, the cross-sectional area A, the membrane thickness L, and the void fraction ϵ_o were 4.96 cm^2, 0.5 μm, and 0.8, respectively. The value of tortuosity factor $\tau_o = 2.5$ was assumed. The BSA molecule (66,700 Da) is a prolate ellipsoid with dimensions of 41 Å×141 Å (Peters, 1985). Using these dimensions, the estimated volume is 110,700 Å^3. The surface area is 14,700 Å^2 (Rodilosso, 1984), and the specific volume of the molecule is 0.733 cm^3/g (Hunter, 1966).

These parameters and experimental results from Robertson and Zydney (1990) were utilized in Eqs. 18 (with $\tau/\tau_o = 1$) and in Eq. 19, and the real root for q_s was determined for two limiting cases where γ was equal to 0 or 0.5. The numerical solution was determined using "fsolve" in Maple V Release 3 (Version 5.3, Waterloo Maple Software, University of Waterloo, Canada) on a 486 DX 50 MHz platform. Error in the solution of the polynomial was on the order of 1×10^{-9} smaller than the polynomial constant.

The calculated solute mass per unit pore surface area M_s^* for both limiting cases in γ are shown in Table 1. As can be seen, the values calculated for $\gamma = 0.5$ are in good quantitative agreement with the surface coverage directly determined by Robertson and Zydney (1990) using radiolabeled BSA throughout the entire range of MWCO membranes. However, the calculated surface coverage values, based on $\gamma = 0$, are approximately one order of magnitude lower in most cases. Using the experimental data for the three cases with intrapore adsorption, a best fit value for γ was determined to be 0.5 ± 0.12. It is thus speculated that $\gamma = 0.5$ is a reasonable assumption for studies involving BSA adsorption on polyethersulfone membranes. Future studies can use this value of γ to determine surface coverage from hydraulic permeability data. For the 1M membrane, Robertson and Zydney (1990) determined that the surface coverage was 0.4 ± 0.25

Table 1. Present Model vs. Results of Robertson and Zydney (1990)

Memb. Properties†			Surface Coverage (μg/cm^2), M_s^*				
MWCO	$S_{p,o}$ (cm^2)	$L_p/L_{p,o}^\dagger$	Exp.†	Random Pore Model $\gamma = 0$	$\tau_o/\tau = 1$ Model $\gamma = 0$	Random Pore Model $\gamma = 0.5$	$\tau_o/\tau = 1$ Model $\gamma = 0.5$
50 K	980	0.68	0.01 ± 0.02	0.01	0.01	0.03	0.03
100 K	470	0.54	0.20 ± 0.08	0.03	0.03	0.08	0.11
300 K	400	0.20	0.45 ± 0.15	0.07	0.08	0.20	0.25
1 M	250	0.06	0.40 ± 0.25	0.19	0.21	0.54	0.65

†Robertson and Zydney (1990).

μg/cm^2, which is approximately one monolayer coverage (~ 0.5 μg/cm^2). The value calculated from this model for the 1M membrane was 0.65 μg/cm^2, which is in excellent agreement with this value.

Robertson and Zydney (1990) used the cylindrical pore model to calculate the radial change from hydraulic permeability data to compare to their experimental surface coverage data. For the 50, 100 and 300 K, and 1M membranes, they determined the radial changes to be 3, 7, 30 and 64 Å, respectively. They compared this to the dimensions of BSA (40 Å × 140 Å) to qualitatively determine how the surface coverage compared the amount of surface adsorption. Clearly, the models presented provide an improved alternative to this method.

Even if the cylindrical pore model was used in the manner outlined here, to calculate solute uptake, it would not maintain the general structure of the hydraulic radius. For the cylindrical pore assumption, the ratio of hydraulic permeabilities is inversely proportional to the hydraulic radius to the fourth power or:

$$\frac{L_p}{L_{p,o}} = \left(\frac{R_h}{R_{h,o}} \right)^4 = \left(\frac{1 - q_s}{1 + \alpha q_s} \right)^4. \tag{20}$$

This model approaches the random pore model as $q_s \rightarrow 0$ and is equivalent to the random pore model only when $\gamma = 0.5$. Since in this study it was determined that $\gamma \approx 0.5$, thus the results for the random pore model with $\gamma = 0.5$ are the same as those determined from the cylindrical pore model.

Conclusions

A physically defensible model is developed for predicting the effect of adsorbed solute particles on the decline of hydraulic permeability in ultrafiltration membranes. Unlike previous models based on the assumption of straight cylindrical pores, the proposed fouling model is free from the assumption of a specific pore geometry. It requires rather a knowledge of the pore surface area and volume of the virgin membrane, which are independently determinable physical properties. It requires further the specific surface area of the solute particles. The model, however, has one (physically meaningful) adjustable parameter γ to account for the loss of pore surface that becomes inaccessible to the flowing fluid due to adsorption. The results can also be easily used to determine the extent of pore surface coverage provided hydraulic permeability data of clean and fouled membrane and solute physical properties are available. The limiting cases of the model (with $\gamma = 0$ and 0.5) were examined and compared to existing data. With $\gamma = 0.5$, the calculations were in good agreement with the mass uptake data for the adsorption of BSA on polyethersulfone membranes (Robertson and Zydney, 1990).

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