



NRC Publications Archive Archives des publications du CNRC

Experimental studies in the dead-end ultrafiltration of dextran: analysis of concentration polarization

Zaidi, S. K.; Kumar, A.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

[https://doi.org/10.1016/S1383-5866\(03\)00207-7](https://doi.org/10.1016/S1383-5866(03)00207-7)

Separation and Purification Technology, 36, April 2, pp. 115-130, 2004-09-15

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=62268522-6003-4711-a052-93ef5fe0ff3f>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=62268522-6003-4711-a052-93ef5fe0ff3f>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.





Experimental studies in the dead-end ultrafiltration of dextran: analysis of concentration polarization[☆]

S.K. Zaidi^b, A. Kumar^{a,*}

^a *Institute for Chemical Process and Environmental Technology, National Research Council of Canada, 1200 Montreal Road, Ottawa, Ont., Canada K1A 0R6*

^b *Department of Chemical Engineering, University of Ottawa, Ottawa, Ont., Canada K1A 9B4*

Received 17 December 2002; received in revised form 24 June 2003; accepted 25 June 2003

Abstract

Considerable theoretical and experimental work has been published to explain the cause of flux decline in the ultrafiltration (UF) of dextran. However, an experimental determination of resistance contributions due to polarization to the overall filtration resistance has not been addressed. Also, the effects of feed concentration and applied pressure on membrane concentration and boundary layer thickness and unsteady-state flux response to a step change in trans-membrane pressure have not been reported. This work reports experimental results of the ultrafiltration of dextran with a fully retentive membrane along with a procedure to determine the contributions of various resistances to filtration. It was observed that the ultrafiltration of dextran was osmotically limited in our work. The contribution of polarization resistance was found to be dependent on applied pressures and initial bulk feed concentrations whereas the boundary layer thickness of polarization was affected by feed concentration alone.

Crown Copyright © 2003 Published by Elsevier B.V. All rights reserved.

Keywords: Ultrafiltration; Concentration polarization; Filtration resistance; Flux decline; Osmotic pressure

1. Introduction

In the ultrafiltration (UF) of macromolecules, permeate flux increases with increasing applied pressure until a critical value is reached where further increase in applied pressure does not increase the permeate flux. This is usually explained either by formation of a gel layer or the build up of concentration due to polarization on the membrane surface by rejected solute. It has also been suggested that a decrease in the

hydraulic driving force, due to additional resistances, is responsible for the decline in permeate flux over time. This decrease could be due to an increase in osmotic pressure, formation of gel layer, concentration polarization, solute adsorption on membrane and pore plugging.

In ultrafiltration, solutes including macromolecules are usually characterized by their propensities for exerting osmotic pressure at the membrane surface. Goldsmith [1] reported this phenomenon and suggested that a degree of osmotic limitation must be taken into account whenever macromolecular solutes are ultra-filtered. Subsequently, several workers have reported that the ultrafiltration of dextran is osmotic

[☆] NRCC No. 46449.

* Corresponding author.

E-mail address: ashwani.kumar@nrc.ca (A. Kumar).

Nomenclature

C	solute concentration (kg/m^3)
D	diffusivity (m^2/s)
J_w	water flux ($\text{m}^3/\text{m}^2 \text{ s}$)
J_s	solvent flux ($\text{m}^3/\text{m}^2 \text{ s}$)
k	mass transfer coefficient (m/s)
ΔP	trans-membrane pressure (kPa)
R_f	filtration resistance (m^{-1})
t	time (s)
x	distance from membrane or gel surface (m)

Greek letters

δ	thickness of polarization layer (m)
μ	solvent viscosity ($\text{kg}/\text{m s}$)
π	osmotic pressure of solute (kPa)

Subscripts

b	bulk
m	membrane surface
x	perpendicular distance from the surface of the membrane

pressure limited [1–4]. Earlier, Clifton et al. [5] explained ultrafiltration flux in hollow fiber modules through osmotic effects. In their work on resistance to the permeate flux in unstirred ultrafiltration of dissolved macromolecular solutions, Nakao et al. [6] calculated the boundary layer concentration of dextran and concluded that this concentration was pressure dependent due to the compressibility of the concentrated boundary layer. They further concluded that no gel layer was found during the ultrafiltration of dextran even with a very high solute concentration of $400 \text{ kg}/\text{m}^3$. Choe et al. [7] reported UF data for dextran for totally retentive membranes in a stirred cell. They measured permeate flux as a function of time for sudden variations of trans-membrane pressures and concluded that during ultrafiltration of dextran, only the polarization layer is formed. This process takes less than a minute and the osmotic pressure model fits the dextran flux data. Choe et al. [7] also studied the flux decline of dextran in UF and concluded that the change in the driving force could be explained in terms of osmotic pressure at the membrane surface.

Furthermore, they found that the mass transfer coefficient variation, with bulk concentration increase in the cell, was insignificant during the batch concentration process.

Karode [8] theoretically predicted the unsteady-state flux behavior using dextran as a model solute. He showed that the concentration at the surface of a membrane is a function of operating parameters and that it was possible to predict the membrane wall concentration as a function of time. Furthermore, theoretical studies on unsteady-state flux response to a step change in trans-membrane pressure showed that a solute, which exerts osmotic pressure but does not form a gel layer, exhibits a gradual flux decline over time. This is followed by a reversible steady-state flux for a sudden increase, followed by a decrease to the initial value of the trans-membrane pressure [9]. Chudacek and Fane [10] also studied the dynamics of polarization using the stirred and unstirred ultrafiltration of dextran and concluded that the polarization time was a function of both concentration and pressure. All of these studies suggested that flux decline in ultrafiltration of dextran could be due to the osmotic pressure at the membrane surface. Considerable theoretical and experimental work has been done over the last 20 years. Most authors have explained the cause of flux decline but none have experimentally determined the contribution of polarization resistance to the total filtration resistance. Also, the effects of feed concentration and applied pressure, on solute concentration over the membrane, boundary layer thickness and unsteady-state flux response to a step change in trans-membrane pressure, have not been discussed. This work reports experimental results for the ultrafiltration of dextran on a fully retentive membrane and a procedure to determine contributions of polarization resistance to total filtration resistance. The effects of step changes in applied pressure on an unsteady-state flux response are also reported.

2. Theory

The separation of solute and solvent takes place at the membrane surface where the solvent passes through the membrane and the retained solute causes the concentration at the membrane surface to increase. This effect is known as concentration polarization.

Concentration polarization accounts for both the gel layer and the solute rich layer at the membrane surface. The relationship between applied pressure and the rate of permeation (flux) for a pure solvent, usually water flowing under laminar conditions in tortuous membrane channels, is modeled using Darcy's law where solvent flux is directly proportional to the effective pressure difference and inversely proportional to the filtration resistance. The constant of proportionality is the inverse of solvent viscosity [11]. Mathematically, this can be written as:

$$J_w = \frac{\Delta P}{\mu R_m} \quad (1)$$

where J_w is the flux of pure water, ΔP the applied pressure, R_m the membrane resistance and μ the solvent viscosity.

If the membrane retains a solute, the driving force and the flow resistance would be modified due to concentration polarization and/or gel layer formation. Permeate flux in such cases can be obtained using the following model reported by Wijmans et al. [12].

$$J_s = \frac{\Delta P - \Delta\pi}{\mu R_f} \quad (2)$$

where J_s is the solvent flux, ΔP the applied pressure, R_f the total filtration resistance, which is equal to the sum of the membrane resistance (R_m) and the resistance offered by the polarization layer (R_p). $\Delta\pi$ is the osmotic pressure difference across the membrane.

In ultrafiltration of macromolecules, membrane resistance might be calculated using Eq. (1). However, this equation is not valid for estimating total filtration resistance for those solutes that exert significant osmotic pressure. There is a need of incorporating the effect of osmotic pressure term in Eq. (1) for accurate determination of various resistances. In order to estimate total filtration resistance, Eq. (2), which includes osmotic pressure term is differentiated with respect to time to give the following equation:

$$\frac{dJ_s}{dt} = \frac{1}{\mu R_f} \left[\frac{d\Delta P}{dt} - \frac{d\Delta\pi}{dt} \right] - \frac{\Delta P - \Delta\pi}{\mu R_f^2} \left(\frac{dR_f}{dt} \right) \quad (3)$$

The second term on the right hand side of this equation can be neglected due to its very small contribution of less than 0.5% in this case. By analysing

post-steady-state transient filtration data obtained by reducing the driving pressure as a function of time, the total filtration resistance can be calculated using the following equation:

$$\frac{dJ_s}{dt} = \frac{1}{\mu R_f} \left[\frac{d\Delta P}{dt} - \frac{d\Delta\pi}{dt} \right] \quad (4)$$

Utilizing unsteady-state permeation data, which was obtained by reducing the applied pressure as a function of time, the total filtration resistance can be calculated by determining the slope of a line obtained by plotting dJ_s/dt versus $d\Delta P/dt$ at a selected applied pressure. The value of $d\Delta\pi/dt$ will be constant during the short duration of transient filtration particularly at the reducing applied pressure.

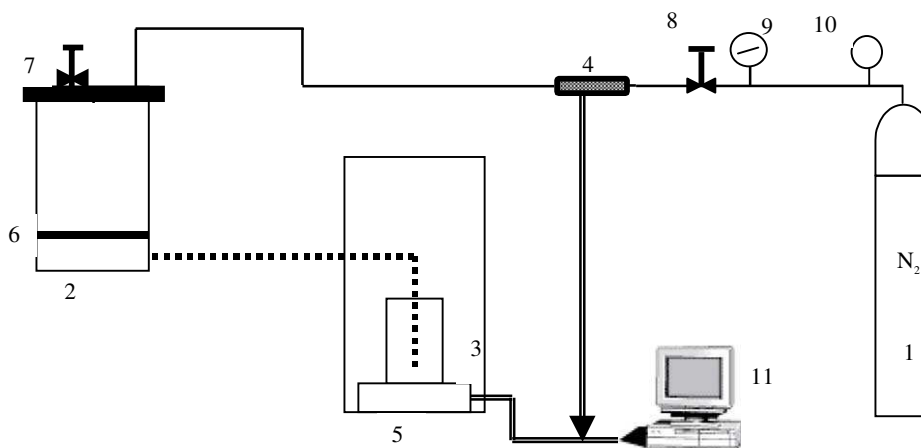
3. Experimental

3.1. Materials and apparatus

The UF membrane used in this work had a nominal molecular weight cut off (MWCO) of 6 kDa and was prepared in the laboratory on a 1079 backing (Tyvek, Supplied by Du-Pont). The membrane casting formulation contained 25% polysulfone (Radel-R Amoco, USA) and 21% polyvinylpyrrolidone (PVP) (Sigma, USA) in *N*-methyl-2-pyrrolidinone (NMP) (Anachemia, USA). The membrane was prepared by the phase inversion method and characterized as described elsewhere [13]. Dextran T40 (Polysciences Inc., USA) with a molecular weight of 39 kDa was used as the standard solute. The dextran concentration in feed solutions was varied from 0.2 to 5 kg/m³. These values were based on reported literature data. Solutions were prepared by adding the required amount of dextran to water followed by stirring for 15–20 min. The concentration of dextran in the feed and the permeate stream was measured on the basis of total carbon (TOC) content. The TOC levels were determined using a TOC Analyser (Shimadzu Corporation, Japan).

3.2. Experimental set-up

Fig. 1 shows a schematic diagram of the experimental set-up. As shown in Fig. 1, all experiments were performed using a commercial ultrafiltration



- | | | | |
|---------------------------------|-------------------|--------------------------|------------------------|
| 1. Gas cylinder | 2. Stirred cell | 3. Beaker | 4. Pressure Transducer |
| 5. Balance | 6. Membrane | 7. Pressure relief valve | |
| 8. Pressure release valve | 9. Pressure gauge | 10. Pressure Regulator | |
| 11. Computer (Data Acquisition) | | | |

Fig. 1. A schematic line diagram of the experimental set-up.

stirred cell unit (Amicon, USA). For each experimental run, the feed chamber was purged with nitrogen. The membrane was set up at the base of the feed chamber and permeate was collected at the bottom of the cell unit. In order to determine the transient flux through the membrane, permeate weight was recorded continuously using a standard balance (SARTORIUS Model No: BP221S). The serial port communication program (RS-232) from the balance was developed using LabVIEW software. A static pressure transducer (Ashcroft, Model No: K5) was installed on the feed side of the cell. The analog output of the static pressure transducer was digitized using a National Instrument PCI 6023E A/D card and a CB-68LP connecting block. A data acquisition system in LabVIEW was developed to synchronize the pressure and mass measurements. The rate of change in flux and pressure were also plotted simultaneously in real-time with the developed software to monitor the transient response.

3.3. Experimental procedure

Initially pure water permeation (PWP) was measured for new membrane. The mass of permeated solvent was recorded every 2 s using the data acquisi-

tion software LabVIEW. An error of less than 0.1% in measuring solvent flux was observed. The membrane resistance for pure water was calculated using Eq. (1). For a given feed solution, flux versus time data was collected at a constant feed pressure until a steady state was reached, i.e. when the flux values became time independent. Once steady state was achieved, the bypass valve (item 8 in Fig. 1) was opened a crack to let the applied pressure decay as a function of time. The unsteady-state filtration data was continuously recorded using the data acquisition system.

3.4. Model parameters

The literature value for the diffusion coefficient of dextran T40 in water at 20 °C was $6.0 \times 10^{-11} \text{ m}^2/\text{s}$ [18]. Several authors [2,15–18] have presented osmotic pressure data for dextran of different molecular weights and reported that there is no significant influence of molecular weight on osmotic pressure. We have used the following relationship between osmotic pressure and solute concentration for calculating osmotic pressure [18]:

$$\Delta\pi = 35.5C_m + 0.752C_m^2 + 76.4 \times 10^{-4}C_m^3 \quad (5)$$

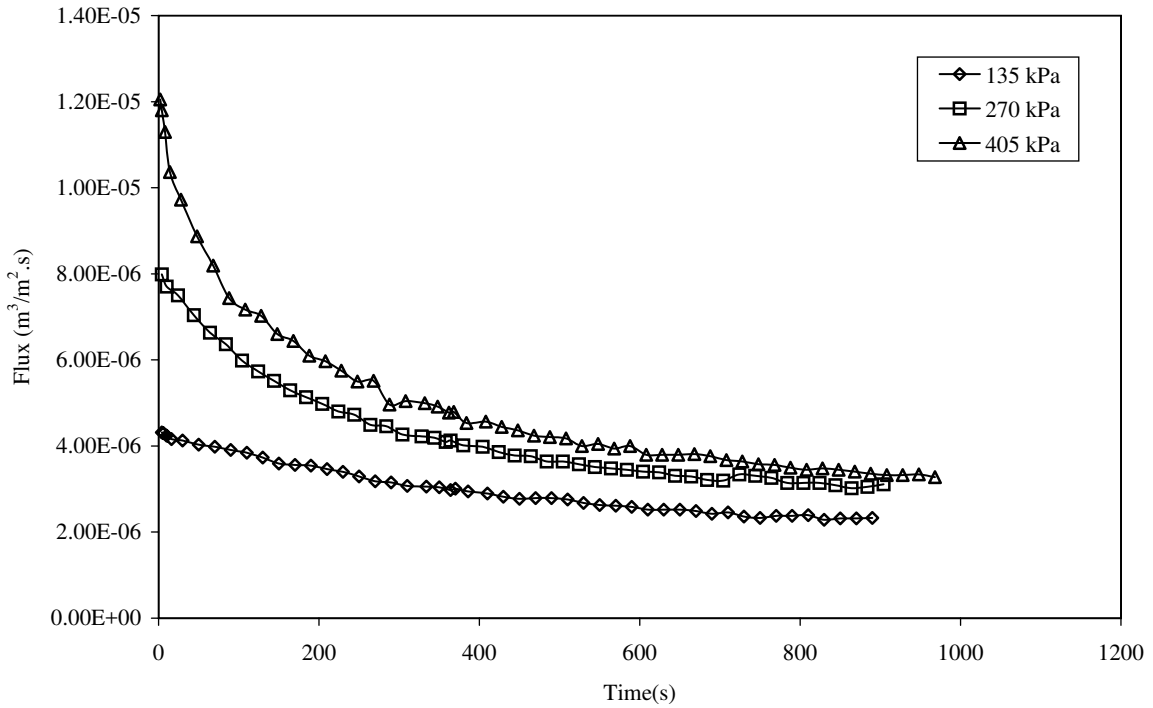


Fig. 2. Variation of permeate flux as a function of time for various values of applied pressure for a bulk dextran concentration of 1 kg/m^3 .

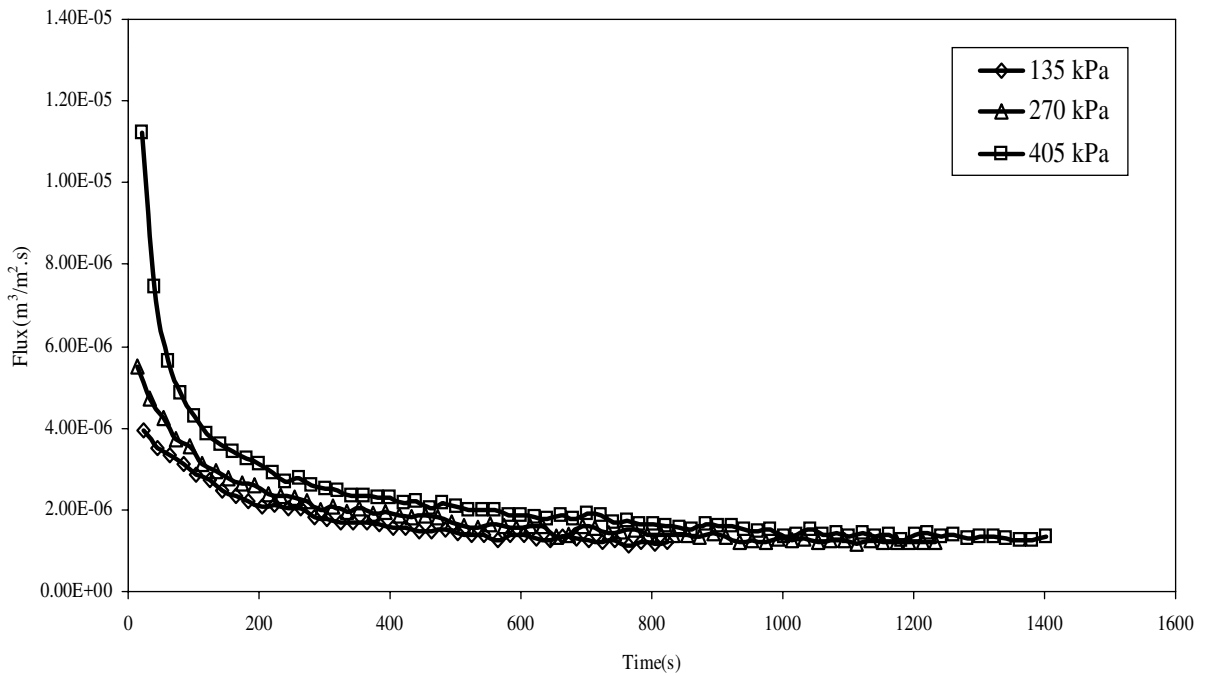


Fig. 3. Variation of permeate flux as a function of time for various values of applied pressure for a bulk dextran concentration of 5 kg/m^3 .

3.5. Data analysis

Solvent permeation data was recorded using the data acquisition software LabVIEW. The data file was created in text by the program on a selected drive. This file was transferred to an Excel worksheet for calculating flux, total filtration resistance, osmotic pressure, concentration of solute in polarized layer, thickness of this layer, and filtration resistance using different models. Concentration at the membrane surface, C_m , was calculated using Eq. (5), which relates osmotic pressure and concentration. Utilizing this value of C_m and the steady-state flux (J_s) the solute concentration profile, as a function of distance perpendicular to the membrane surface, was estimated using the film theory.

4. Results and discussions

Permeate flux data for dextran T40 solutions are shown in Figs. 2 and 3 for feed concentrations of 1 and

5 kg/m^3 at applied pressures of 135, 270 and 405 kPa, respectively. It is clear from these figures that the permeate flux initially drops rapidly followed by a gradual decrease. This sudden drop in flux at the beginning of the experiment is explained with the osmotic pressure model. A build up of the polarization layer at the membrane surface leads to an increase of the solute concentration at the membrane surface. Consequently, the osmotic pressure rises rapidly, resulting in a decrease of the net driving force. This high concentration at the membrane surface is due to the high rejection and the low diffusion coefficient of dextran that considerably reduces the rate of back transport. This leads to a further increase in the concentration on the surface.

Fig. 3 shows flux as a function of time for a 5 kg/m^3 dextran solution. Note that compared to the two cases with lower dextran concentrations (0.2 and 1 kg/m^3), steady-state values of flux are independent of applied pressure. This phenomenon is clearly shown in Fig. 4 where flux is plotted as a function of applied pressure for different bulk feed concentrations. The steady-state values of flux for the lower feed

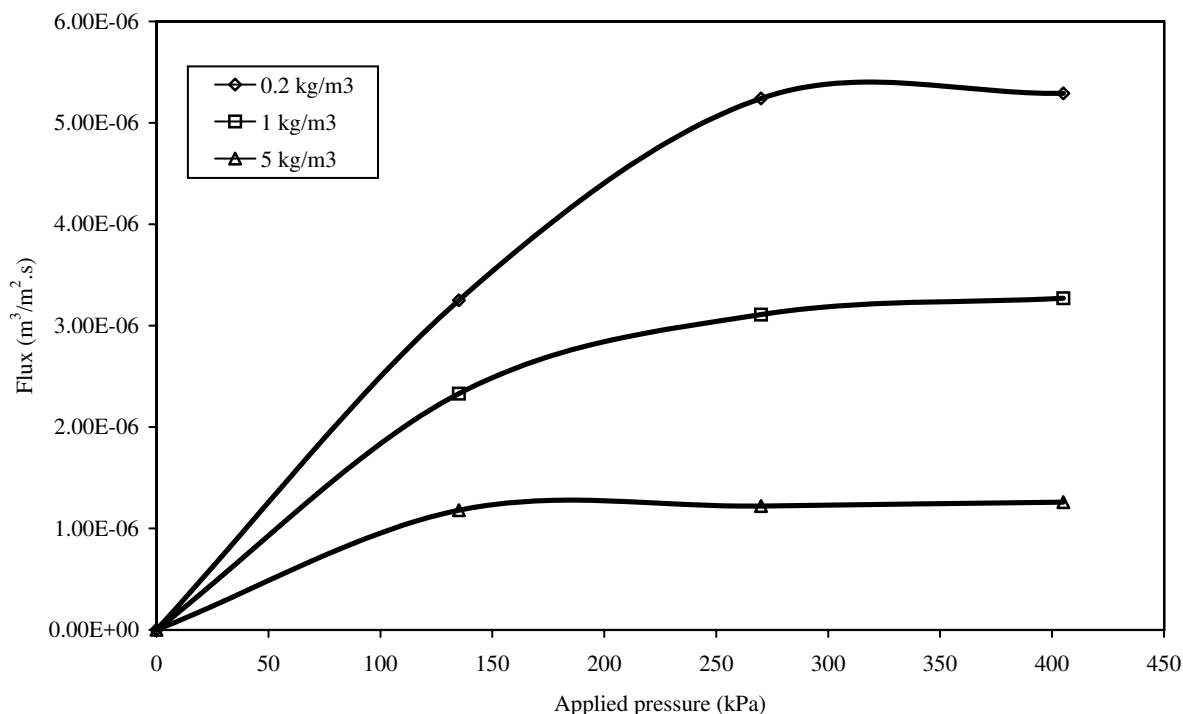


Fig. 4. Steady-state permeate flux as a function of applied pressure for different feed concentration of dextran.

concentration (0.2 kg/m^3) at different applied pressures range between $(3.25\text{--}5.30) \times 10^{-6} \text{ m}^3/\text{m}^2 \text{ s}$ while for the higher feed concentration (5 kg/m^3) these values range between $(1.18\text{--}1.30) \times 10^{-6} \text{ m}^3/\text{m}^2 \text{ s}$. It is interesting to note that the UF of dextran was found to satisfy the case of only osmotic pressure limited flux even if flux, at higher concentration, was found to be pressure independent. These observations are similar to many reported in [3,18]. At lower applied pressure and lower bulk feed concentration, the flux indeed changes with a change in applied pressure however, at higher pressure and higher concentration flux appears to be pressure independent. This is probably due to higher osmotic pressure build up, which leads to relatively constant driving force for different applied pressures. The effects of bulk concentration were also shown in Fig. 4. It is well known that an increase in the bulk concentration of the solution decreases permeate flux. Higher concentrations lead to higher osmotic pressure, hence lower fluxes are observed. Furthermore, higher concentrations may be giving higher polarized layer resistance, which is

inversely proportional to flux. However, the trends of the flux versus time curves are identical when bulk concentration increased at a fixed pressure, as shown in Figs. 2 and 3.

Fig. 5 shows the variation of the unsteady-state permeate flux as a function of reducing applied pressure for initial feed concentration of 5 kg/m^3 . This figure clearly explains the concept of polarization layer build up and its dependence on applied pressure and feed concentration. It is clearly noted from this figure that pressure decay from any higher value is slightly lower than the flux at the same pressure when pressure decay started from a lower initial value. This is due to the accumulation of more solute at the membrane surface when ultrafiltration was done using higher initial solute concentrations and explains the pressure independent flux concept. However, a negative flux was not observed. It simply means that the osmotic pressure was never higher than the applied pressure. These transient data presented in Fig. 5 can be further analyzed by plotting the dJ_s/dt versus $d\Delta P/dt$ as shown in Fig. 6. The slopes of these straight lines were used

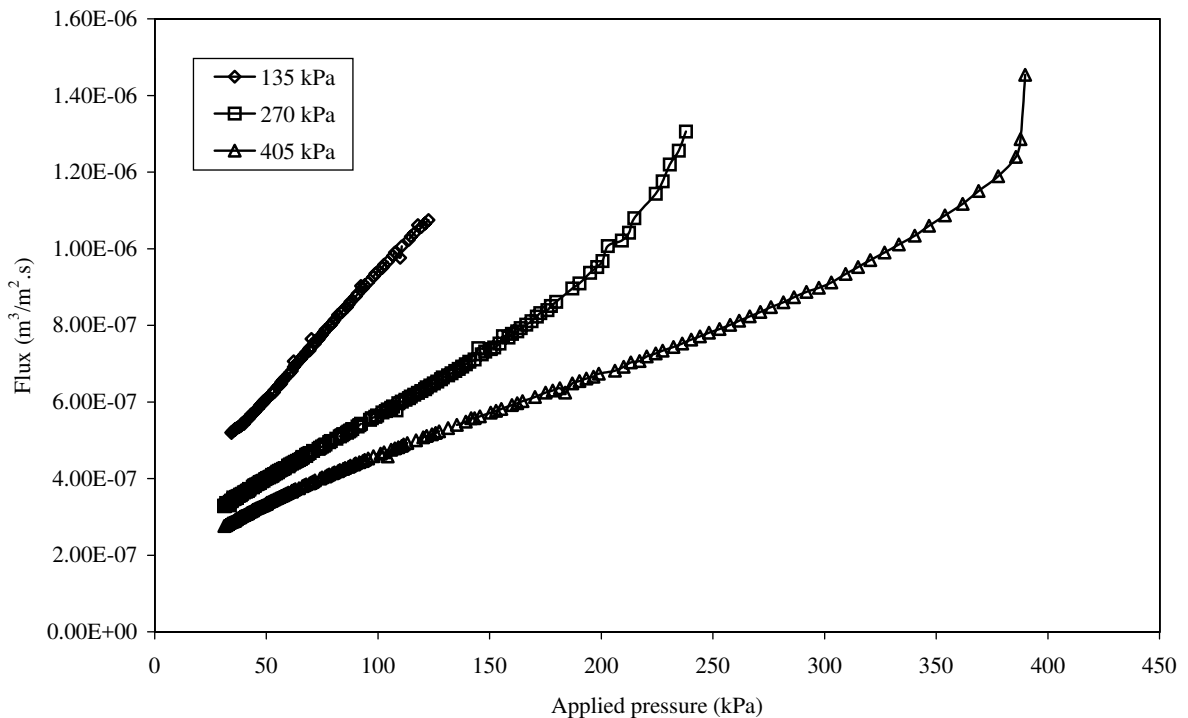


Fig. 5. Post-steady-state transient permeate flux as a function of reducing applied pressure for bulk dextran concentration of 5 kg/m^3 .

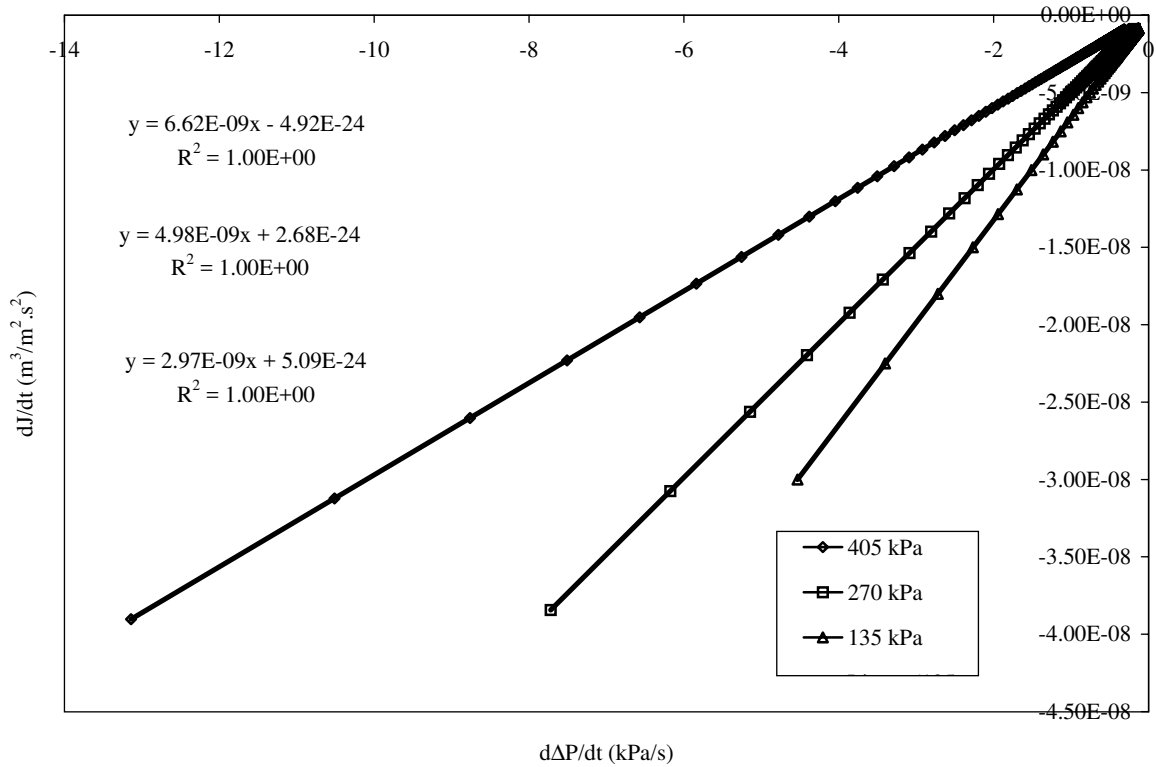


Fig. 6. Post-steady-state transient flux (dJ_s/dt) vs. transient applied pressure ($d\Delta P/dt$) for the data presented in Fig. 5.

Table 1

Filtration resistance analysis of dextran T40 at initial bulk concentration of 5 kg/m^3 and different applied pressures

ΔP (kPa)	$R_f = R_m + R_p (\times 10^{-14})$	$R_m (\times 10^{-13})$	$R_p (\times 10^{-14})$	Percentage due to R_p
135	1.37	3.54	1.01	74.2
270	1.83	3.61	1.48	80.2
405	3.06	3.63	2.71	88.1

Table 2

Filtration resistance analysis of dextran T40 at initial bulk concentration of 1 kg/m^3 and different applied pressures

ΔP (kPa)	$R_f = R_m + R_p (\times 10^{-14})$	$R_m (\times 10^{-13})$	$R_p (\times 10^{-13})$	Percentage due to R_p
135	0.51	3.61	1.61	29.6
270	1.02	3.61	6.73	64.6
405	1.50	3.64	11.5	75.7

Table 3

Filtration resistance analysis of dextran T40 at initial bulk concentration of 0.2 kg/m^3 and different applied pressures

ΔP (kPa)	$R_f = R_m + R_p (\times 10^{-13})$	$R_m (\times 10^{-13})$	$R_p (\times 10^{-13})$	Percentage due to R_p
135	3.83	3.51	0.22	8.32
270	4.55	3.57	1.04	21.5
405	7.06	3.61	3.55	48.9

to calculate total filtration resistance as described earlier [14]. Filtration resistance was found to be a function of applied pressure and solute concentration. The experimental and estimated values of actual filtration resistance, membrane resistance and resistance offered by polarization are given in Tables 1–3. Detailed filtration data is listed in these tables for different applied pressures and initial bulk solute concentrations. It is clear from these tables that the membrane resistance (R_m) was relatively constant with a standard deviation of only 1.2%. The percentage of resistance offered by polarization during the ultrafiltration of dextran (R_p) of the total filtration resistance (R_f) however, was found to be dependent on applied pressures as well as initial bulk solute concentrations. It was assumed that there was no pore plugging or adsorption of solute on the membrane.

Table 4 shows the observed steady-state membrane rejection (R) for the entire range of pressure and concentration values studied in this work. As can be seen from this table, the steady-state solute rejection rate was always greater than 90%. It was found to be a

Table 4

Steady-state rejection (%) of dextran T40 at different applied pressures and bulk concentrations (C_b)

ΔP (kPa)	0.2 kg/m ³	1 kg/m ³	5 kg/m ³
135	97.0	95.9	95.1
270	94.3	93.4	91.2
405	92.1	90.9	90.1

function of applied pressure and feed concentration. As shown in Fig. 7, steady-state dextran rejection decreased with an increase in flux. Maximum observed rejection was for lowest concentration and pressure. This observation clearly demonstrates that for the entire flux range rejection values are influenced by concentration polarization. This is further confirmed by a higher observed rejection for the 0.2 kg/m³ solute concentration at 135 kPa when compared to the 5 kg/m³ solute concentration at an applied pressure of 405 kPa.

Figs. 8 and 9 show the unsteady-state permeate fluxes as a function of time in response to a sudden pressure change for dextran T40 with different initial

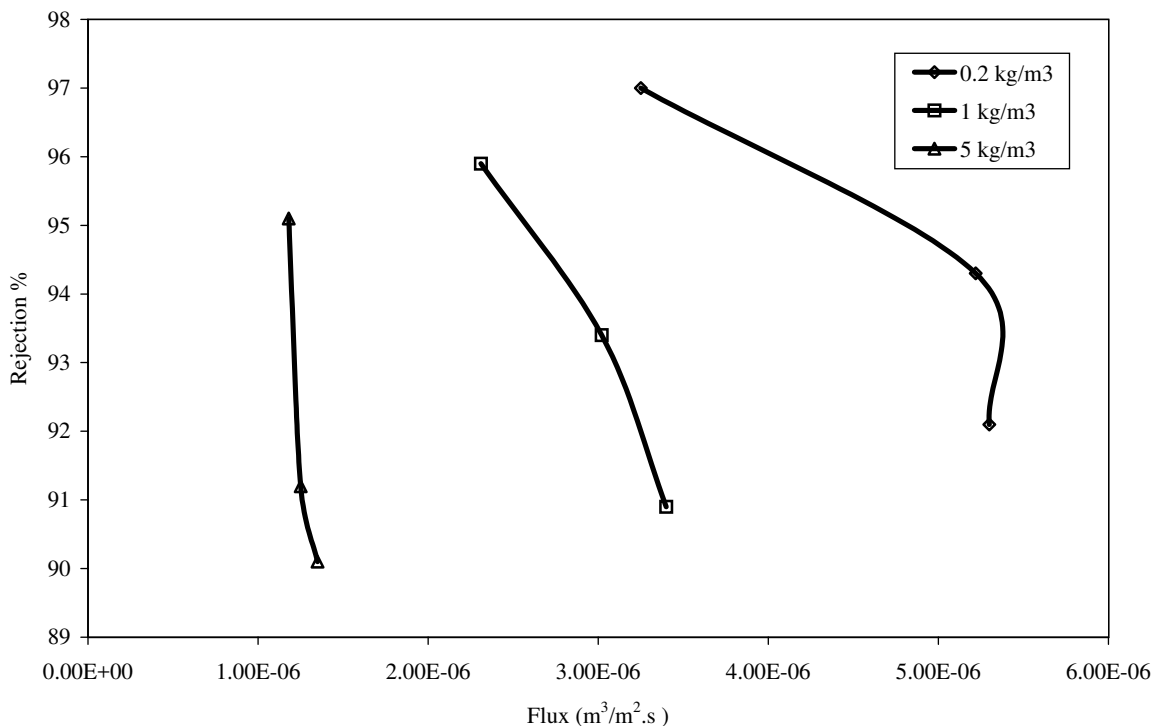


Fig. 7. Steady-state dextran rejection as a function of permeate flux.

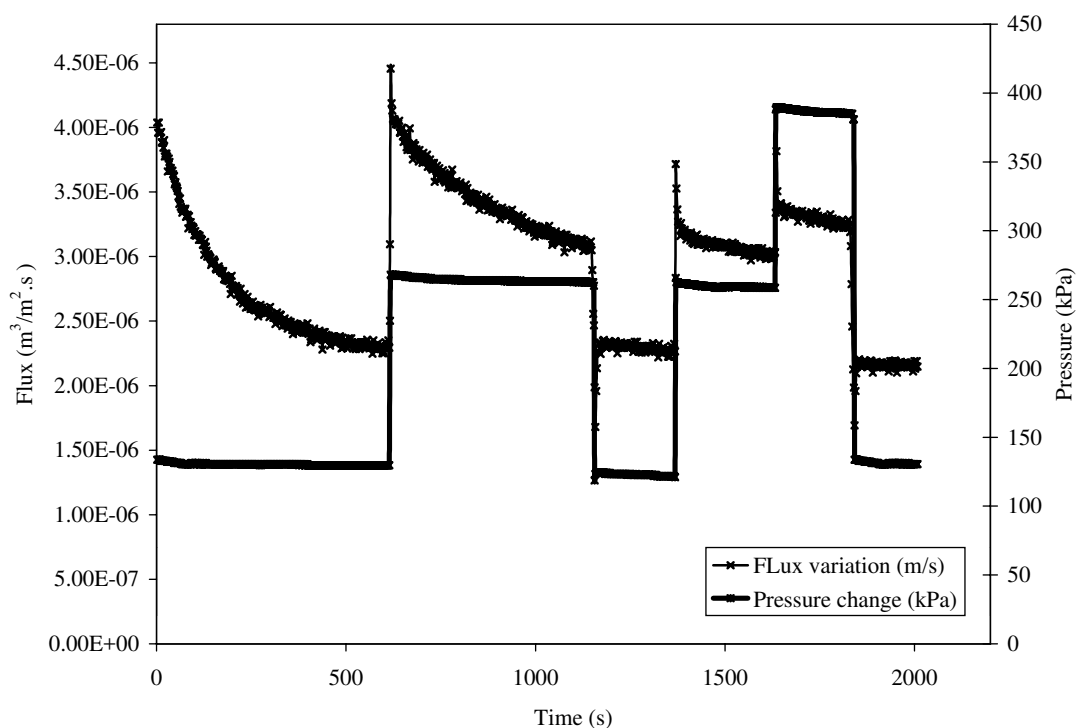


Fig. 8. Unsteady-state permeate flux as a function of time in response to a sudden change of applied pressure (pressure cycle) for a bulk dextran concentration of 1 kg/m^3 .

bulk feed concentrations. The sudden change of pressure was defined as a pressure cycle when pressure was changed according to the following sequence:

135 kPa \rightarrow 270 kPa \rightarrow 135 kPa \rightarrow 270 kPa
 \rightarrow 405 kPa \rightarrow 135 kPa.

The starting trans-membrane pressure ($t = 0$) was set to 135 kPa for all three cases. After the steady state was reached, ΔP was increased to 270 kPa once steady state was achieved again the pressure was dropped to 135 kPa and this procedure was repeated according to the defined pressure cycle. This procedure was used to predict unsteady-state flux response. As can be seen from Figs. 8 and 9, for all solute concentrations, an increase in ΔP results in a corresponding increase in the steady-state permeate flux. However, at the same time, an unsteady behavior was observed, when the pressure was increased from 135 to 270 kPa and then later returned to the lower pressure. For the lower feed concentration of 1 kg/m^3 , it was found that

the 100% increase of the applied pressure increased steady-state permeate flux by only 35–50%. Moreover this increment in steady-state flux was further decreased by 2–5% when the pressure was increased by additional 50%, from 270 to 405 kPa. In this cycle, decreasing the pressure back to 135 kPa resulted in a reversible decrease in the permeate flux to a value slightly lower than the steady-state value obtained initially at 135 kPa. This flux behavior is well predicted by the osmotic pressure model. The doubling of applied pressure does not lead to the doubling of permeate flux. Here, an increase in applied pressure is partly compensated by an increase in osmotic pressure and similarly a 50–100% decrease in applied pressure does not result in a proportionate decrease in the permeate flux as evidenced in Figs. 8 and 9.

At both pressure changes, the concentration gradient at the membrane surface varied rapidly. However, there was a gradual decrease in flux during the entire experiment, which is again due to an increase of the bulk concentration with time. These experimental

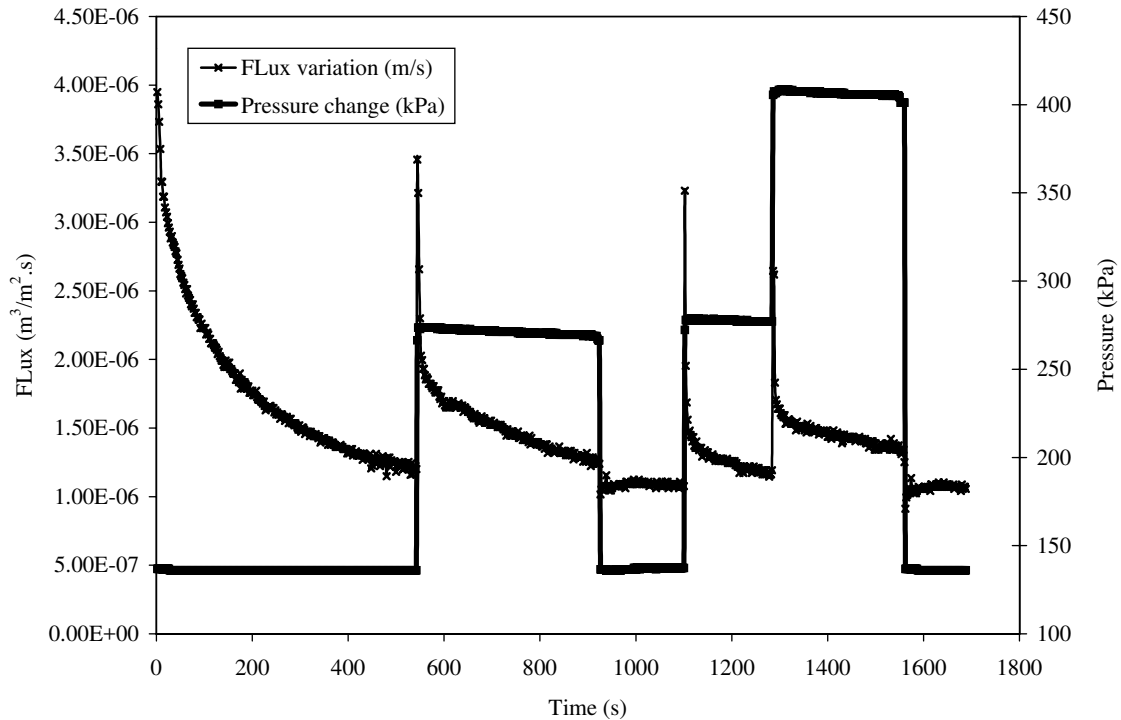


Fig. 9. Unsteady-state permeate flux as a function of time in response to a sudden change of applied pressure (pressure cycle) for a bulk dextran concentration of 5 kg/m^3 .

observations are in agreement with theoretical studies reported earlier [9].

The response of the flux to the sudden pressure changes provides additional information, which is indicative of the sole presence of a polarization layer. It was shown experimentally that the steady-state flux varies with a change in applied pressure, which clearly indicates that only a polarization layer is present. However, for the higher feed concentration of 5 kg/m^3 , if the fluxes have comparable values for both pressures or the flux change is not very high, like the previous cases, this in itself does not provide proof of the presence of a gel layer. Using experimentally measured permeate flux at given bulk solute concentration and applied pressure, followed by the determination of total filtration resistance as defined in Tables 1–3, the osmotic pressure of an accumulated solute at the membrane surface can be calculated using Eq. (2). This calculated π_w is plotted as a function of the unsteady pressure for bulk solute concentrations of $1\text{--}5 \text{ kg/m}^3$ at different initial applied pressures in Figs. 10 and 11.

This analysis shows that for all bulk solute concentration and applied pressures, the osmotic pressure of dextran at the membrane surface was a function of applied pressure, which is clearly indicative of osmotic limited ultrafiltration.

Wijmans et al. [12] and Van Oers [18] have used a simple model for representing a flux reduction due to concentration polarization. The osmotic pressure, π_w , is determined by the solute concentration (C_m) at the membrane surface. It is assumed that the increase in concentration at the membrane surface can be calculated according to the film theory. First π_w was calculated using Eq. (2), then C_m , could be calculated from the concentration–osmotic pressure relationship given in Eq. (5). Using this value of C_m and steady-state flux, J_s , a solute concentration profile as a function of distance perpendicular to the membrane surface can be estimated using the film theory and the following equation [19–21]:

$$C_x = C_b + (C_m - C_b) \exp\left(\frac{-J_s x}{D}\right) \quad (6)$$

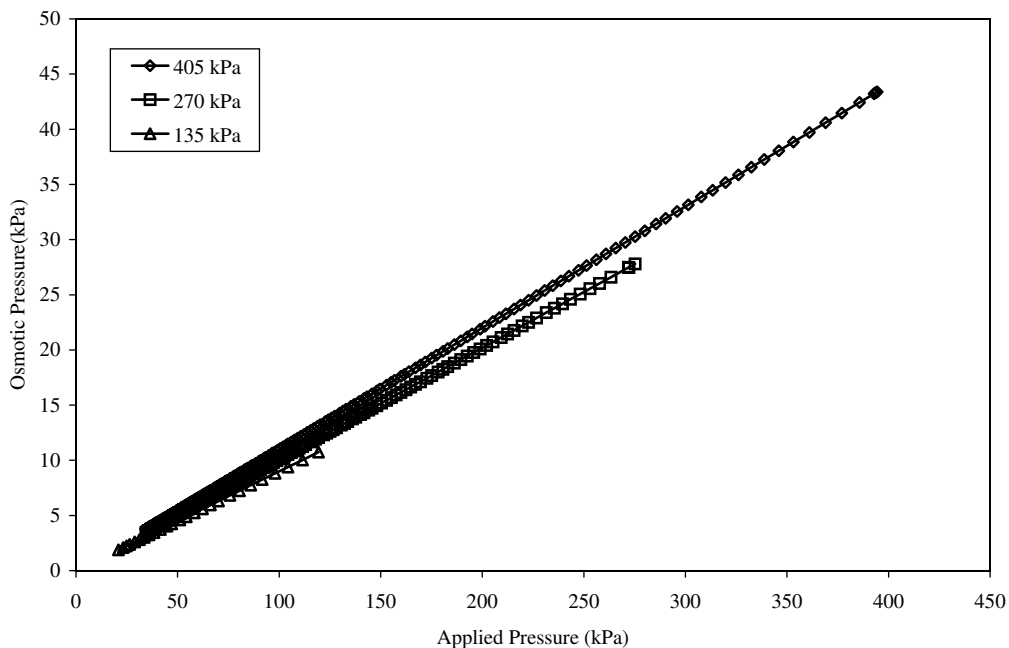


Fig. 10. Osmotic pressure at the membrane surface (π_w) vs. applied pressure for dextran bulk concentration of 1 kg/m³.

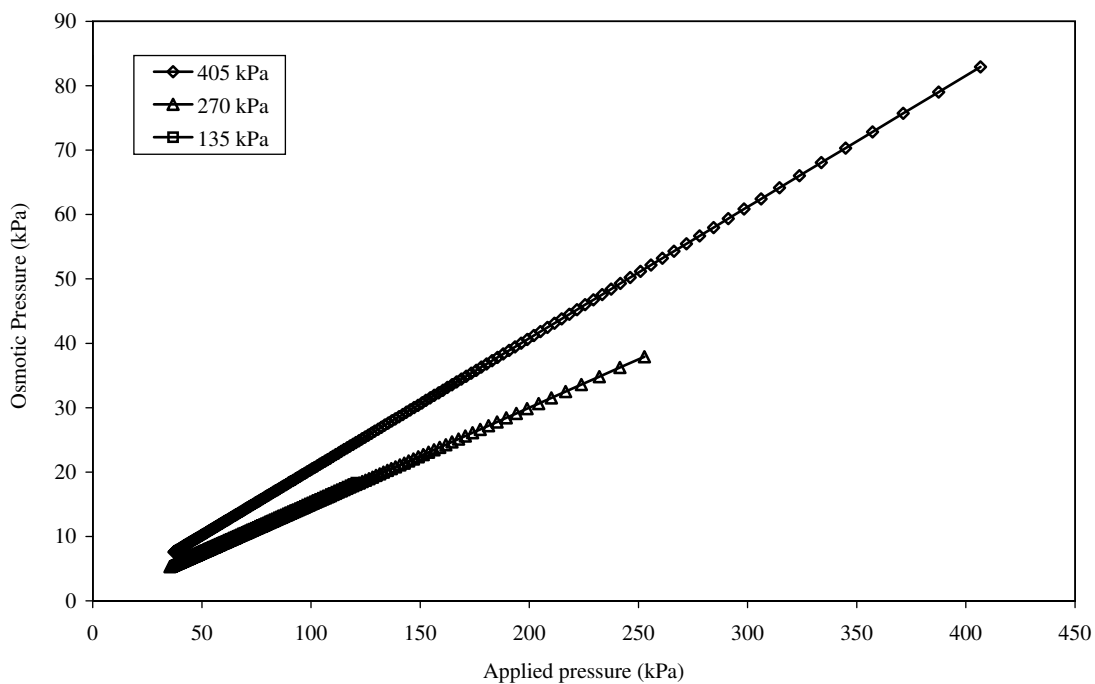


Fig. 11. Osmotic pressure at the membrane surface (π_w) vs. applied pressure for dextran bulk concentration of 5 kg/m³.

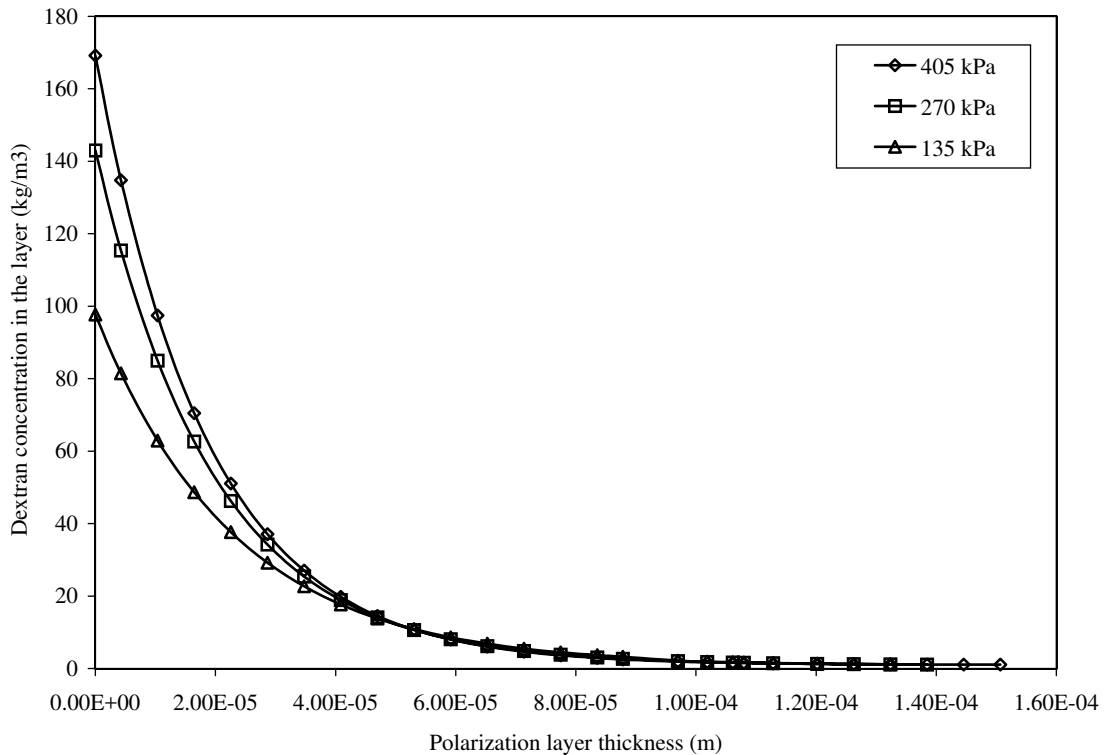


Fig. 12. Dextran concentration profile as a function of distance perpendicular to the membrane surface for three different applied pressures for dextran bulk concentration of 1 kg/m^3 .

where D is diffusivity and is calculated using the literature correlation. The boundary layer thickness (δ) can then be estimated as that value of x at which the solute concentration becomes equal to the bulk solute concentration.

Figs. 12 and 13 show the steady-state solute concentration profile within the polarization layer for two different feed concentrations (1 and 5 kg/m^3) for different applied pressures (135 , 270 and 405 kPa). These concentration profiles were plotted as a function of distance from the membrane surface. It is clear from these figures that solute concentration increases sharply at the initial stage of UF and flux drop is drastic during this stage. Since the solute concentration at the membrane surface is a function of time, applied pressure and bulk solute concentration, the solute concentration increase at the membrane surface would be more rapid with higher applied pressures and bulk solute concentrations.

The boundary layer thickness was plotted as a function of bulk solute concentration for different applied pressures in Fig. 14. It is evident that the boundary layer thickness is independent of applied pressure but varies with bulk solute concentration. Figs. 15 and 16 show the variation of steady-state solute concentration on the membrane surface and osmotic pressure exerted by the solute present in the polarization layer as a function of bulk solute concentration at different applied pressures, respectively. It is clear from these figures that at higher applied pressures and bulk solute concentrations, the concentration of solute accumulated in the polarization layer is higher. This is due to the higher rejection and lower back diffusion of solute in bulk solutions. Furthermore, variation of concentration with applied pressure also justifies the concept of osmotic limited behavior of the solute. Since osmotic pressure is a function of solute concentration, it also varies with bulk solute concentration accordingly.

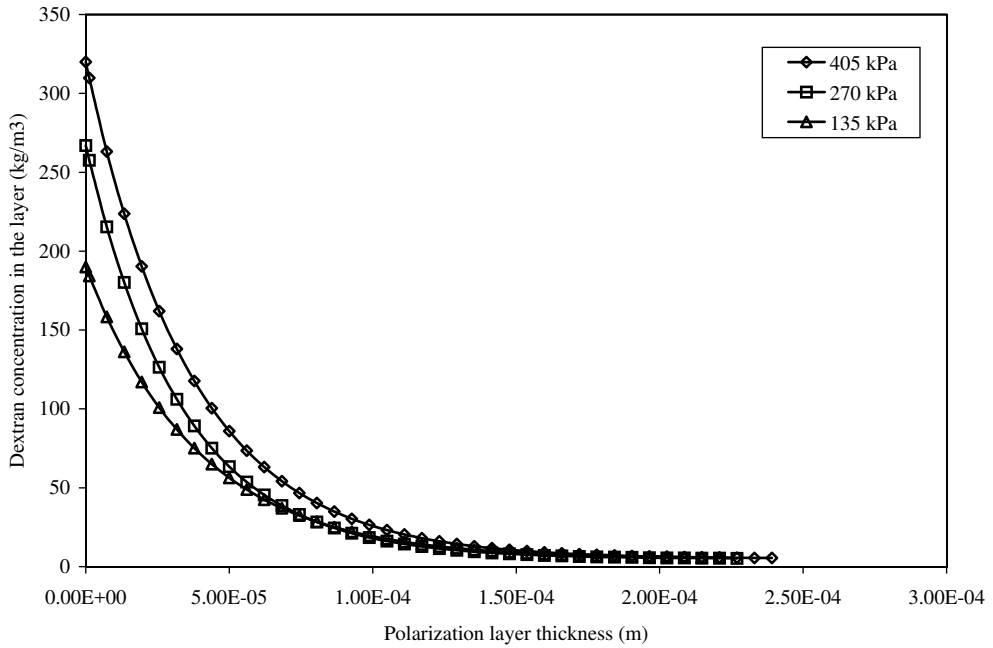


Fig. 13. Dextran concentration profile as a function of distance perpendicular to the membrane surface for three different applied pressures for a dextran bulk concentration of 5 kg/m³.

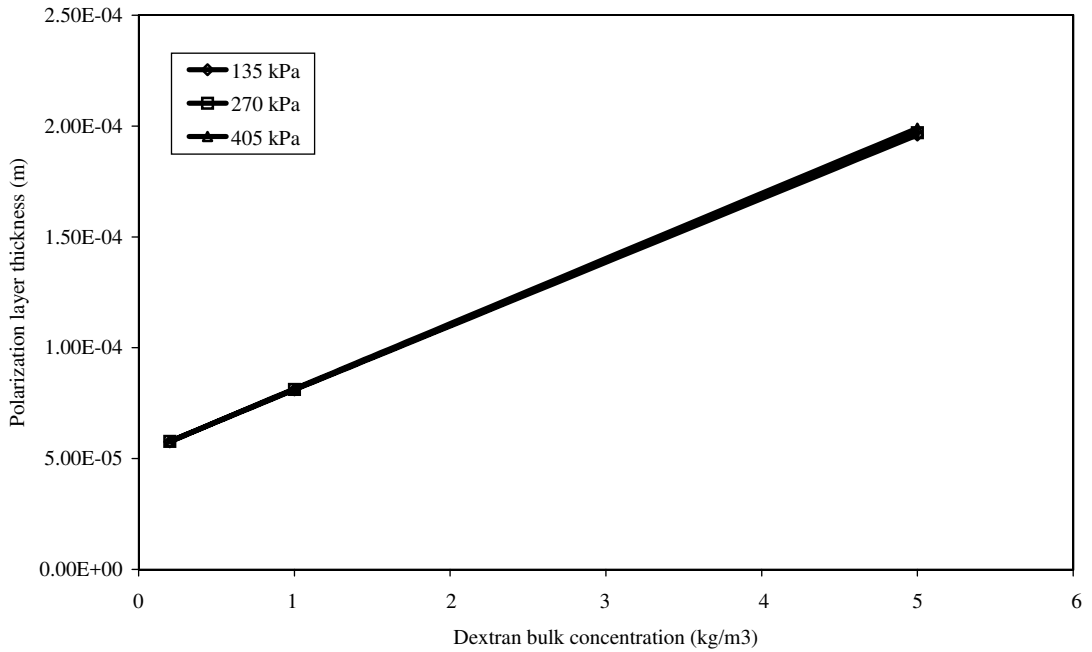


Fig. 14. Effect of dextran bulk concentration on boundary layer thickness at different applied pressures.

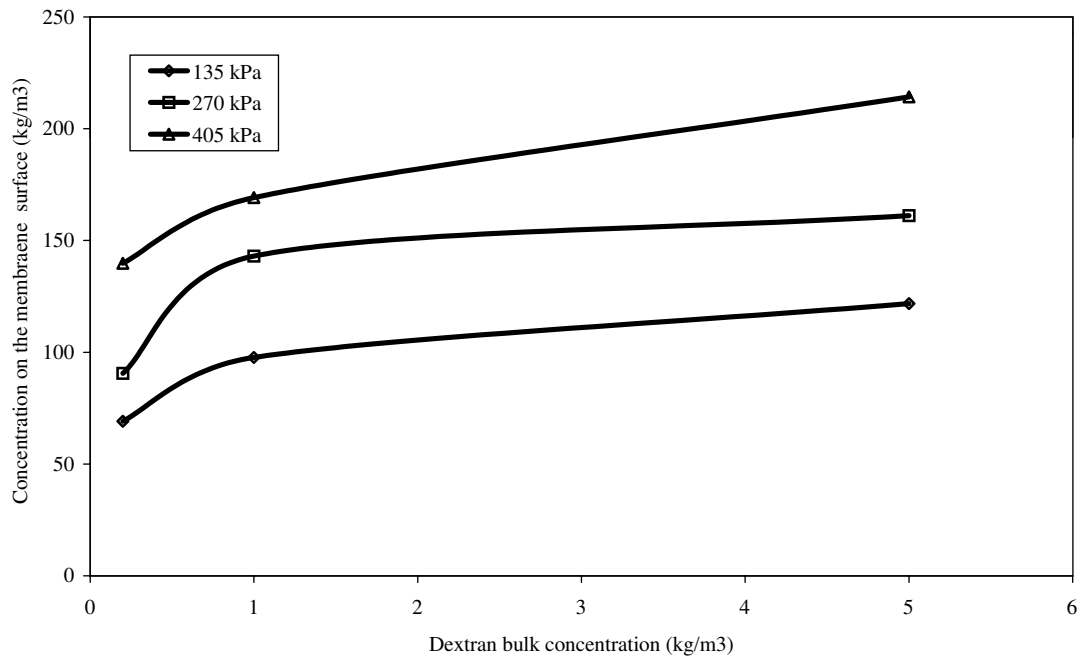


Fig. 15. Dextran concentration at membrane surface as a function of dextran bulk concentration at different applied pressures.

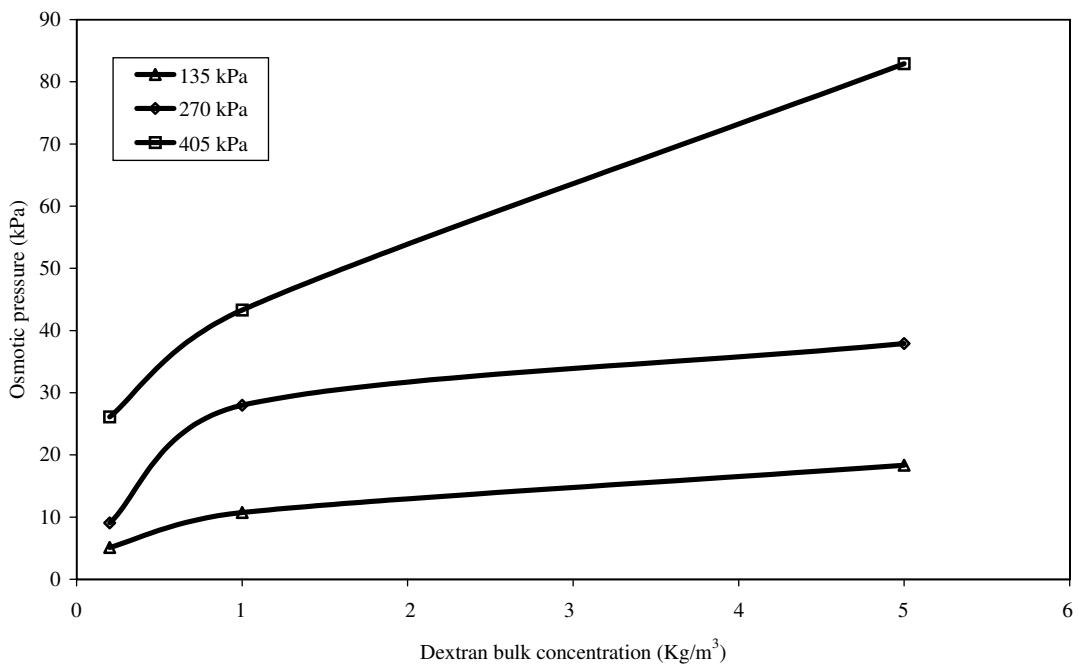


Fig. 16. Osmotic pressure exerted by dextran accumulated at membrane surface as a function of dextran bulk concentration at different applied pressures.

5. Conclusions

In the ultrafiltration of dextran, flux declines gradually with time followed by a reversible steady-state value. In pressure cycling experiments, permeate flux values did not change proportionately for a sudden increase followed by a decrease of trans-membrane pressure. It was concluded that the UF of dextran was osmotically limited and no gel layer was formed even in the case of a pressure independent flux regime for the concentration range studied in this work. The contribution of polarization resistance to actual filtration resistance was dependent on applied pressures and initial bulk solute concentrations. It was further demonstrated that the thickness of the polarization layer in the ultrafiltration of dextran solutions could be significantly large. It was also concluded that the thickness of the polarization layer is a function of the bulk solute concentration and a higher bulk concentration led to a thicker polarization layer. The solute concentration in the polarization layer and the osmotic pressure were also dependent on the applied pressure and bulk solute concentration.

Acknowledgements

Authors wish to express their sincere thanks to Dr. Sandeep Karode for helpful discussions before starting this experimental work and Mr. Deepak Kirplani for help in LabView programming.

References

- [1] R.L. Goldsmith, Macromolecular ultrafiltration with microporous membrane, *Ind. Eng. Chem. Fundam.* 10 (1971) 13.
- [2] J.G. Wijmans, S. Nakao, J.W.A. van den Berg, F.R. Tolestra, C.A. Smolders, Hydrodynamic resistance of concentration polarization boundary layer in ultrafiltration, *J. Membr. Sci.* 22 (1985) 117.
- [3] G. Jonsson, Boundary layer phenomena during ultrafiltration of dextran and whey protein solutions, *Desalination* 51 (1984) 61.
- [4] P. Paradanos, J. de Abajo, J.G. de la Campa, A. Hernandez, A comparative analysis of flux limit models for ultrafiltration membranes, *J. Membr. Sci.* 108 (1995) 129.
- [5] M.J. Clifton, N. Abidine, P. Aptel, V. Sanchez, Growth of the polarization layer in ultrafiltration with hollow fibre membranes, *J. Membr. Sci.* 21 (1984) 233.
- [6] S. Nakao, J.G. Wijmans, C.A. Smolders, Resistance to the permeate flux in unstirred ultrafiltration of dissolved macromolecular solutions, *J. Membr. Sci.* 26 (1986) 165.
- [7] T.B. Choe, P. Masse, A. Verdier, M.J. Clifton, Flux decline in batch ultrafiltration: concentration polarization and cake formation, *J. Membr. Sci.* 26 (1986) 1–15.
- [8] S.K. Karode, A new unsteady state model for macromolecular ultrafiltration, *Chem. Eng. Sci.* 55 (2000) 1769.
- [9] S.K. Karode, Unsteady state flux response: a method to determine the nature of the solute and gel layer in membrane filtration, *J. Membr. Sci.* 188 (2001) 9.
- [10] M.W. Chudacek, A.G. Fane, The dynamics of polarization in unstirred and stirred ultrafiltration, *J. Membr. Sci.* 21 (1984) 145.
- [11] A.S. Ward, Liquid filtration theory, in: M.J. Matteson, C. Orr (Eds.), *Filtration: Principle and Practices*, Marcel Dekkar, New York, 1987, p. 135.
- [12] J.G. Wijmans, S. Nakao, C.A. Smolders, Flux limitation in ultrafiltration: osmotic pressure model and gel layer model, *J. Membr. Sci.* 20 (1984) 115–124.
- [13] M.M. Dal-Cin, C.M. Tam, M.D. Guiver, Polysulfone membranes V. Polyphenylsulfone (Radel R)-polyvinylpyrrolidone membranes, *J. Appl. Polym. Sci.* 54 (1994) 783.
- [14] S.K. Zaidi, S.K. Karode, D. Kirpalani, A. Kumar, A new method for identifying osmotically limited and gel layer controlled pressure independent flux in ultrafiltration, *Can. J. Chem. Eng.* (2003), in press.
- [15] K.A. Granath, B.E. Kvist, Molecular weight distribution analysis by gel chromatography on sephadex, *J. Chromatogr.* 28 (1967) 69.
- [16] H. de Balmann, R. Nobrega, The deformation of dextran molecules: causes and consequences in ultrafiltration, *J. Membr. Sci.* 40 (1989) 311.
- [17] A.G. Ogston, N. Preston, Macromolecular compression of dextran, *Biochem. J.* 183 (1979) 1.
- [18] C.W. Van Oers, M.A.G. Vorstman, W.G.H.M. Muijselaar, P.J.A.M. Kerkhof, Unsteady-state flux behavior in relation to the presence of a gel layer, *J. Membr. Sci.* 73 (1992) 231–246.
- [19] G.B. Vanden Berg, I.G. Racz, C.A. Smolders, Mass transfer coefficient in cross flow UF, *J. Membr. Sci.* 47 (1989) 25.
- [20] C. Bhattacharjee, S. Datta, A numerical simulation for the prediction of flux and rejection during ultrafiltration in unstirred batch cell using variable diffusivity concept, *Sep. Purif. Technol.* 24 (2001) 13–22.
- [21] A.L. Zydney, Stagnant film model for concentration polarization in membrane systems, *J. Membr. Sci.* 130 (1997) 275–281.