Korean J. Chem. Eng., **21**(3), 556-561 (2004)

Analysis of Continuous Stirred Ultrafiltration Based on Dimensional Analysis Approach

Chiranjib Bhattacharjee†

Department of Chemical Engineering, Jadavpur University, Calcutta-700032, India
(*Received 22 May 2003 • accepted 24 October 2003*)

Abstract−In this study an attempt has been made to obtain a dimensional analysis based empirical model of ultrafiltration process under stirred condition, which for a given membrane will predict the permeate flux and the rejection during the dynamic as well as the steady state phases of operation from the process conditions applied, viz. pressure drop, stirrer speed, bulk concentration of the filtered species etc. A dimensional analysis by Rayleigh's method was performed and the obtained dimensionless groups were related with the help of experimentally obtained data in this study, by non-linear regression employing Levenberg and Marquardt technique. Two equations have been obtained, one for the prediction of flux and other for the rejection. The computed results are found to be in good agreement with the experimental data obtained in this study during the ultrafiltration of PEG-6000 by cellulose acetate membrane and the absolute average deviation was found to be within less than 7%.

Key words: Ultrafiltration, Flux, Rejection, Dimensional Analysis, Simulation, Experimental Data

INTRODUCTION

Ultrafiltration (UF) is primarily a size exclusion-based pressure-driven membrane separation process. Typical rejected species include sugar, biomolecules, polymers and colloidal particles, which makes it highly suitable for application in industries like pulp and paper, food processing, pharmaceuticals, paints, etc. However, the major impediment to any such large-scale industrial application lies in a problem inherent to the process [Belfort et al., 1994; Cheryan, 1986; Zeman and Zydney, 1996; Tarleton and Wakemen, 1993]. Membrane fouling, which leads to decline of flux with time reduces the production rate and makes the process uneconomic in terms of the time consumed since the system has to be stopped frequently to restore the flux by back flushing. So, the major challenge faced by any proposed model of the ultrafiltration process is its ability to predict this dynamic nature of permeate flux and concentration under any operating condition. Various attempts have so far been made towards the theoretical modeling of the fouling phenomenon and thereby predicting flux and rejection as a function of time. In most of the research papers published in various journals, one of the three following basic concepts has been suggested to explain the fouling phenomenon: (a) Resistance in Series theory, (b) Gel Polarization theory, and (c) Osmotic Pressure theory. Finally, a model is then proposed on that basis with an essentially theoretical approach. But, since the actual mechanism of fouling has not yet been ascertained, such theoretical models naturally fall short of the mark where predictions of results of actual ultrafiltration operations are necessary.

In the past two or three decades substantial experimental effort has been made to investigate effects of various parameters on flux decline and mechanisms of membrane fouling. While data of time-dependent fluxes have been collected from numerous ultrafiltration experiments under various conditions, not much progress has been made in understanding of the fundamental mechanisms of membrane fouling. This results in difficulty regarding the theoretical prediction of flux and rejection in such separation process.

Various attempts have so far been made regarding the theoretical modeling of the fouling phenomenon and hence thereby predicting flux and rejection as a function of time. Trettin and Doshi [1980] developed their theory essentially based on gel layer formation and proposed their integral model which was an effort in the unification of macromolecular ultrafiltration theories with classical filtration theory. This model differentiates substantially compared to the Shen and Probstein [1977] model. Experiments with unstirred batch cell using bovine serum albumin (BSA) solution were performed to testify this model [Shen and Probstein, 1977]. A summary of governing transport and adsorption phenomena in porous membrane ducts under isothermal conditions was given in the review article by Belfort and Nagata [1985].

The development of mathematical models has provided a conceptual framework for understanding the phenomena responsible for flux decline. Most of the equations used to characterize ultrafiltration systems are extrapolations of models previously developed for other filtration systems. For example, the osmotic pressure model was originally developed for reverse osmosis (RO) membranes [Goldsmith, 1971], while resistance models are very similar to those used in classical filtration [Ruth, 1935]. On the other hand, the gel model was specifically developed for the ultrafiltration of macromolecules [Nakao et al., 1979]. Various works on the simulation of an ultrafiltration process have been reported in the literature recently. Simulation of an ultrafiltration process in case of bovine serum albumin in hollow-fiber membranes is reported by Secchi et al. [1999]. Prediction of mass transfer coefficient and thereby simulating flux and rejection has been discussed by Minnikanti et al. [1999]. The common flow modules, namely, rectangular channel, tubular and radial cross flow ultrafiltration and microfiltration were investigated by perceiving membrane fouling as a dynamic process from non-equilibrium to equilibrium [Song, 1998]. A computer simulation was discussed by Lebrun et al. [1989] to calculate the membrane performance data for a rectangular slit configuration. A very good

†To whom correspondence should be addressed.
E-mail: c_bhatta@rediffmail.com

work in formulating the concentration polarization phenomenon was reported by Song and Elimach [1995]. The model applies to concentration polarization of non-interacting particles in cross-flow filtration system. A significant work regarding modeling of concentration polarization and depolarization with high frequency back pulsing was reported by Redkar et al. [1996].

Some recent work has been reported on micellar-enhance ultrafiltration (MUCF) by Park et al. [1997]. MUCF is a separation process using surfactants and membranes which can remove dissolved organic solutes or multivalent ions from water. Iritani and Mukai [1997] have investigated the flux and rejection in membrane filtration from physicochemical aspects. It was shown that the physical nature of the deposited cake-layer has an important effect on the filtration rate and rejection. Furthermore, it was shown that electrical nature of the particles and solvent density play an important role in deciding filtration rate. Recently, a glass-ball inserted module design has been suggested by Kim and Kim [2003] to enhance the membrane flux. Effectiveness of this module was tested for three different modes of filtration: normal dead-end filtration, vortex flow filtration and enhanced vortex flow. It was found that for glass ball inserted membrane module, permeate flux tended to increase with increase in feed flow rate. A water treatment application of ultrafiltration process coupled with coagulation process has been reported very recently by Jung and Kang [2003]. This work is based on detailed experimental investigation with an objective to remove natural organic matter (NOM). Various other applications of ultrafiltration are being reported continuously in various journals.

Most of the works reported in literature are either related with dynamic or steady state analysis/simulation, and all these works are essentially based on any one of the three basic classical models or any combination of that. Most of these works are not general in nature and applies to a specific case of a solute-membrane combination. In fact, the exact modeling of a membrane separation process like ultrafiltration is very difficult from its microscopic point of view, and establishment of any model has to be corroborated based on indirect experimental evidence. Due to this reason a semi-empirical approach has been followed in this study.

In the present study, instead of going into understanding the mechanism of ultrafiltration, a semi-empirical approach has been explored, taking into consideration the process of fouling not by its origin but by the way it is manifested in experimental results. The best tool to handle such an approach is dimensional analysis. The functional relationship between the various groups has been studied based on the experimental data obtained during this study. Two non-linear models have been developed for prediction of flux and rejection by non-linear regression technique of Levenberg and Marquardt. The simulated results are found to be in good agreement with the experimental data obtained with cellulose acetate membrane of 5000 MWCO filtering PEG-6000 solution. In all the cases, predicted values are found to be within ±10% of the corresponding experimental data.

THEORY

In this study a semi-empirical approach has been followed to correlate the flux with other parameters. During ultrafiltration in continuous stirred cell the volumetric flux declines with time mainly due to the effects of concentration polarization, reversible/irreversible fouling or pore blocking, resistance build-up over the membrane (gel formation) or any combination of these effects depending upon the type of solute - membrane combination used. Since the exact mechanism of flux decline is difficult to predict a priori and it varies from system to system, a dimensional analysis approach has been used to correlate flux.

1. Model Development

The variables involved may be listed as follows:

1-1. Independent Variables

Bulk concentration (C_b), stirrer speed (N), pressure differential (ΔP), viscosity of solution (μ), density of solution (ρ), impeller diameter (D_s), time (t).

1-2. Dependent Variable

Permeate volumetric flux (J), Rejection (R).

It is desired to obtain two different relations, one for permeate flux and the other for rejection. The dimensional analysis has been done by Rayleigh's method, whereby the two relations are assumed to be of the form:

$$J=(C_b)^a (N)^b (\Delta P)^c (\mu)^d (\rho)^e (D_s)^f (t)^g \quad (1)$$

$$R=(C_b)^a (N)^b (\Delta P)^c (\mu)^d (\rho)^e (D_s)^f \quad (2)$$

It may be noted that time (t) has not been considered as a variable in the relation for rejection (R). This is because during experimental runs, rejection was not found to vary appreciably with time. By the usual method of equating the indices of the fundamental dimensions for both sides of the equations, the following dimensionless forms have been obtained from Eqs. (1) and (2) respectively:

$$(J/ND_s)=\alpha(C_b/\rho)^a (\Delta P/\rho D_s^2 N^2)^c (ND_s^2\rho/\mu)^d (tN)^g \quad (3)$$

$$R=\beta(C_b/\rho)^x (\Delta P/\rho D_s^2 N^2)^y (ND_s^2\rho/\mu)^z \quad (4)$$

The dimensionless groups may be denoted as follows:

(J/ND_s)	Dimensionless flux (N_J)
(C_b/ρ)	Dimensionless bulk concentration (N_{Cb})
$(\Delta P/\rho D_s^2 N^2)$	Modified Power number (N_{Po})
$(ND_s^2\rho/\mu)$	Stirrer Reynolds number (N_{Re})
(tN)	Dimensionless time (N_t)

EXPERIMENTS

The schematic diagram of the experimental set up is shown in Fig. 1. The main objective of the experiments was to observe the various factors, which affect the flux decline phenomena. For this reason, experiments were conducted on continuous mode. Since a stirred batch cell has been used for the purpose of experimentation, permeate had to be pumped back into the cell to maintain the bulk concentration constant. A high pressure metering pump was used to recycle the permeate. This pump also served the purpose to pressurize the ultrafiltration cell, instead of using any compressor or compressed nitrogen. A damper was also used in the recycle loop to eliminate any pressure fluctuation arising out of the operation of the metering pump.

1. Materials

Polyethelyne glycol (PEG-6000) in molecular weight range (6000-7000) was obtained from Sisco Research Laboratories Pvt. Ltd.,

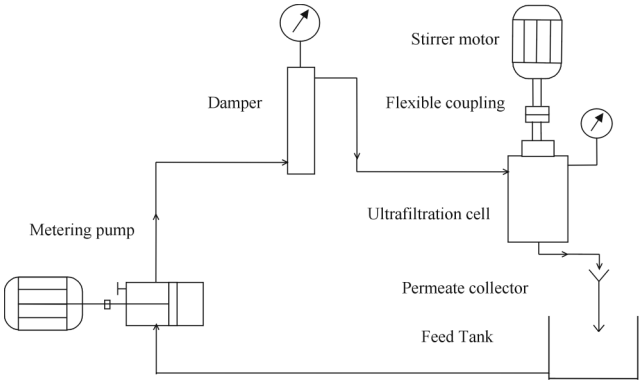

Fig. 1. Schematic diagram of experimental setup.

Bombay, India. Cellulose acetate complex membrane (PLCC 090 05, asymmetric, molecular weight cut-off 5000) was imported from Millipore Corporation, Bedford, USA. The membranes are usable in pH range 2-10; they are hydrophilic, resistant to temperatures up to 90 °C and have low adsorption characteristics.

2. Apparatus

A stirred batch ultrafiltration cell was fabricated with the following specifications: material SS 316, useful volume 450 ml, filtered diameter 76 mm, effective filtration area 2.64×10^{-3} m^2, maximum testing pressure 3.5 MPa, with a mechanical stirring facility (stirrer diameter 56 mm) using a variable speed motor. This cell was used in a continuous mode by recycling the permeate, as mentioned earlier.

3. Analysis

Concentration of PEG solution was measured by refractive index calibration method. An optical refractometer with an accuracy of ±0.001 on reading and ±0.0001 with eye estimation was used in the experiments. The relationship between the refractive index (RI) and concentration was found to be as follows:

$$C=7.226\times10^{3}RI-9.607\times10^{3} \quad (5)$$

here C is the solute concentration in kg/m^3. The viscosities and densities were correlated to concentration of PEG-6000 solution at 30 °C and the following equations were obtained.

$$\mu=(0.801236+1.47403\times10^{-2}C+6.26114\times10^{-5}C^2+4.66925\times10^{-7}C^3)/1000 \quad (6)$$

$$\rho=(0.9976+2.776\times10^{-4}C-9.822\times10^{-7}C^2)\times1000 \quad (7)$$

4. Design of Experiments

Experiments were designed so that the effects on flux and rejection of three major independent variables, i.e. bulk concentration (20, 50, 70 and 90 kg/m^3), pressure differential (552, 689 and 827 kPa) and stirrer speed (5.41, 7.5 and 8.83 r.p.s.) can be properly understood. During experiments, two variables were held constant while the third was varied to get an exact picture of the dependence. The permeate was collected in a measuring cylinder as a function of time and the total collected volume after every 15 minutes were noted. From this data the volumetric flux (J) was calculated by using the relationship:

$$J=\frac{1}{A}\frac{dV}{dt} \quad (8)$$

The permeate concentration was also noted at 15 minutes interval with the help of an optical refractometer through the refractive index calibration method. The feed concentration was also ascertained by measuring its refractive index. Thus the experiments constitute 4×3×3×9=324 data sets for flux and 4×3×3=36 data sets for rejection (as rejection was observed to be time-independent).

RESULTS AND DISCUSSIONS

1. Study of the Dependencies of the Dimensionless Groups

The data obtained from the abovementioned experiments have been used to calculate the values of the various groups obtained in the dimensionless analysis, and the trends of the variation of the dimensionless flux with the groups containing the independent variables have been studied graphically. Out of the 324 data-points for flux and 36 for rejection, about 60% of these data were used for correlation development and remaining 40% for model validation. Effect of power number on dimensionless flux group at different bulk concentration and stirrer Reynolds number are shown in Fig. 2. As is evident from the figure, dimensionless flux shows a clear increasing tendency with Power number. Also, from the study of the relative position of the different series it can be said that it also shows a definite increase with decreasing bulk concentration. Effects of Reynolds number on dimensionless flux at different bulk concentration and at same value of power number are shown in Fig. 3. Dimensionless flux shows a definite increasing trend with stirrer Reynolds number. Also, it is observed that it decreases with increase in bulk concentration at constant power number, a fact that is also observed from Fig. 2.

Effect of power number with rejection at different values of Reynolds number and bulk concentration is shown in Fig. 6. It is observed from the above figure that rejection (R) decreases with increasing values of power number which is reasonable because power number contains the pressure differential variable and it is natural that rejection will decrease with increase in pressure drop for polymeric macromolecular solutes. At high pressure, this type of the solute may squeeze pass through the pores of the membrane, thus decreasing the rejection value.

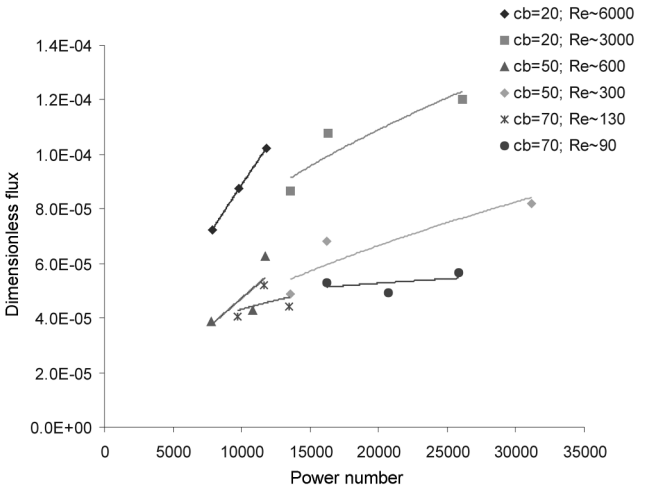

Fig. 2. Variation of dimensionless flux with power number at constant bulk concentration and Reynolds number at steady state.

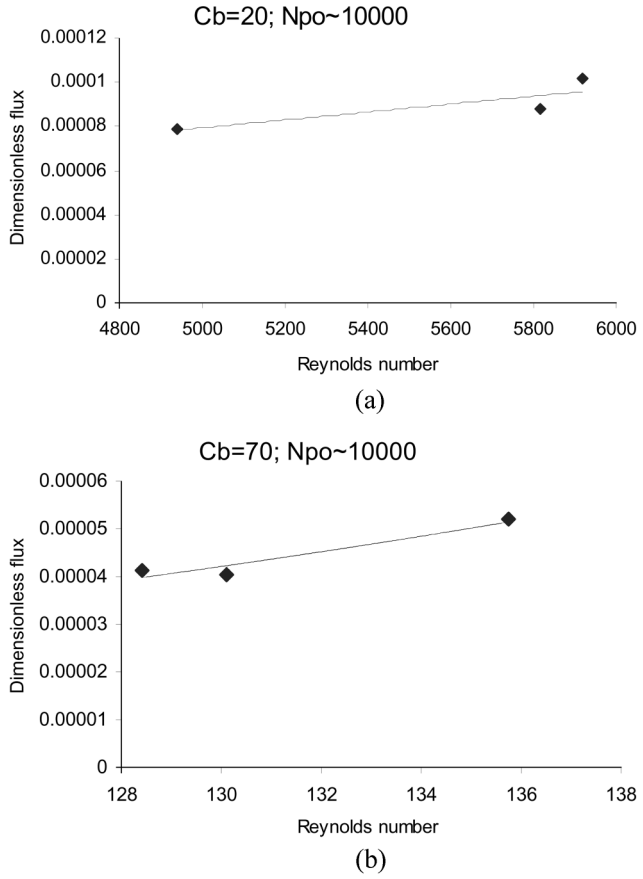

Fig. 3. Variation of dimensionless flux with Reynolds number at constant bulk concentration and Power number under steady state conditions.

2. Regression Analysis

In this study, software has been developed to fit a nonlinear function of the form:

$$y = y(\bar{x}; \bar{a}) \tag{9}$$

where $\bar{a}$ is a vector of regression parameters and $\bar{x}$ is a vector of independent variables. Obviously then $\bar{x}^T = (x_1, x_2, x_3, \ldots x_L)$ and $\bar{a}^T = (a_1, a_2, a_3, \ldots a_M)$, where L represents number of multiple independent variable and M are the number of regression constant. It is assumed that a set of N tabulated values of $(x_1, x_2, x_3, \ldots x_L)$ (independent variables) versus y (dependent variable) is available. It is to be noted that the number of data points (N) must be greater than M+1 (thus N≥M+1). The program uses the Levenberg-Marquardt (LM) algorithm for finding the parameter values, which minimizes the sum of squares of the errors. The developed software has the capability to handle both multiple nonlinear regression, as well as nonlinear regression with single independent variable and multiple regression constants, defined by any user defined model. A detailed explanation of this method can be found, for example, in the book by Press et al. [1992]. The function (sometimes called the "chi square" or the "merit function") that is minimized with the help of this algorithm is as follows:

$$S(a) = \sum_{i=1}^{N} [y_i - y(\bar{x}_i; \bar{a})]^2 \tag{10}$$

where N is the number of data points, $\bar{x}_i$ denotes the x data points vector, y_i denotes the y data points, and $y(\bar{x}_i; \bar{a})$ is an arbitrary non- linear model evaluated at data point i. This merit function simply measures the agreement between the data points and the parametric model; a smaller value for the merit function denotes better agree- ment.

Two different implementations of the LM method are included. The LM technique is an iterative solution method, which usually converges very rapidly, except when the Hessian matrix becomes nearly singular. In such cases, the algorithm switches to the steepest descent method, the convergence of which can be very slow. A nearly singular Hessian matrix often indicates that there are more parameters in the model than are justified by the data. In case of slow convergence, it is recommended that the iterations should be stopped and statistical analysis has to be performed to verify the correctness of the number of model parameters. If there are more parameters than really needed, the 95% confidence interval for most of the parameters will tend to be much larger than the parameter value itself. In this study, the 95% confidence interval remains well within the bound for all the experiment. The summary of the results obtained while fitting Eq. (3) are given in Table 1:

So the model Eq. (3) can be written with the parameter values obtained from above as:

$$N_J = 1.883\text{E-}07 (N_{Cb})^{0.279} (N_{Po})^{0.523} (N_{Re})^{0.303} (N_t)^{-0.026} \tag{11}$$

In a similar manner, co-relation for rejection (R) was derived as:

$$R = 1.4539029 (N_{Cb})^{0.023} (N_{Po})^{-0.093} (N_{Re})^{0.049} \tag{12}$$

3. Comparison Between Predicted and Experimental Results

Once the parameter values of the model have been obtained, Eq. (11) is capable of predicting the permeate flux during the dynamic and steady state phases of operation under any given combination of input variable values, provided the membrane characteristics and the filtered species as well as the carrier remains the same. In the following figures a comparison is made between the results predicted by the model and those obtained experimentally.

Table 1. Regression results for predicting N_J

Nonlinear regression (mrqmin)		
Model: $N_J = a*N_{Cb}^b * N_{Po}^c * N_{Re}^d * N_t^e$		
Variable	Ini guess	Calc value
a	1.80E-07	1.883E-07
b	0.2	0.2785399
c	0.5	0.5227169
d	0.3	0.3031904
e	−0.0	−0.0263961
Nonlinear regression settings		
Max # iterations=300		
Tolerance=0.0001		
Precision		General
R^2=0.9338178		Sample size=297
R^2adj=0.9329112		# Model vars=5
Rmsd=3.91E-07		# Indep vars=4
Variance=4.618E-11		# Iterations=186
Chi-Sq=1.348E-06		

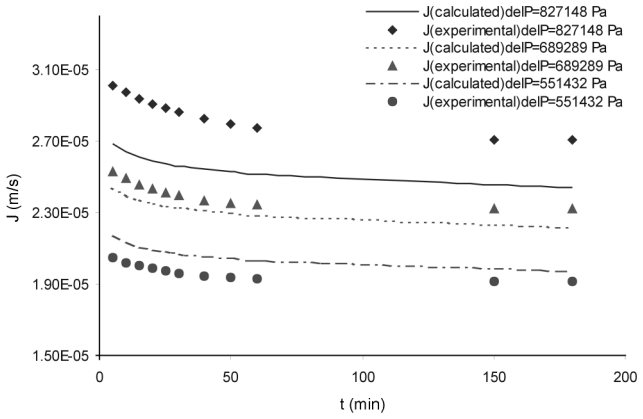

Fig. 4. Comparison between predicted and experimental values of flux plotted against time for different ΔP at constant C_b= 20 Kg/m^3 and constant N=8.829 rps.

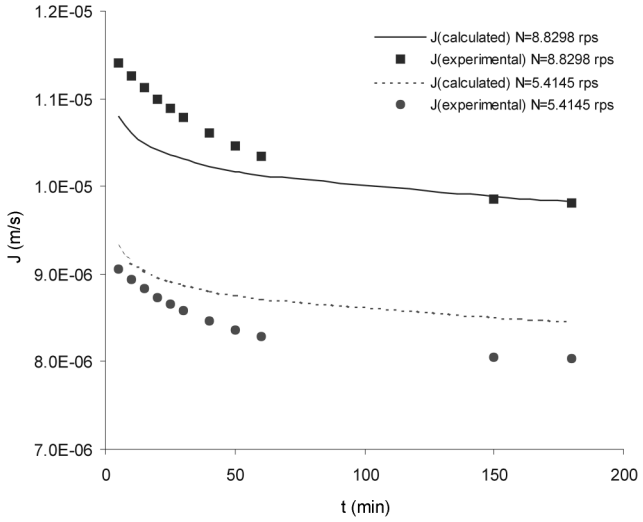

Fig. 5. Comparison between predicted and experimental values of flux plotted against time for different N at constant C_b= 70 Kg/m^3 and constant ΔP=551432 Pa.

As seen in the Figs. 4 and 5, the predicted values of flux are very near to those obtained experimentally. However, more importantly, it is clearly seen that the trend of variation of flux with time, which basically characterizes the fouling phenomenon predicted by the model, is very similar to that exhibited by the experimental values. At the same time, as is expected, the flux is found to increase with increasing values of ΔP (Fig. 4), and also with N (Fig. 5) while the other parameters remain constant.

The prediction from the model Eq. (12) has been shown in Fig. 6, in addition to the experimental data, as reported earlier. It was noted in the experimental results that the dependency of rejection on Reynolds number is not very well defined. This is the reason why only the variation of rejection with Power number has been studied here. In Fig. 6, it is found that the experimental and predicted values of rejection are very much comparable both in terms of precision and trend of variation. Absolute average deviations were calculated for both flux and rejection and were found to be 6.1% and 6.9% respectively.

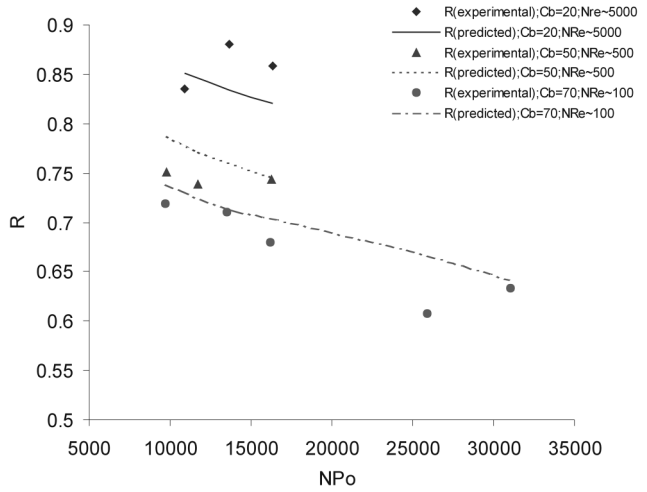

Fig. 6. Comparison between predicted and experimental values of rejection varying with Power number at constant bulk concentration and Reynolds number.

CONCLUSION

It cannot be denied that for a given membrane operating with a given species, the obtained model has been quite accurate in predicting the permeate flux, especially during the initial dynamic stage of operation where membrane fouling comes to play. Moreover, it may be noted that the model equation obtained here does not contain parameters characteristic to the membrane e.g. pore diameter, membrane hydraulic resistance etc. So, it is planned as an extension of work to carry out experimental runs for different membranes operating with different filtered species. It may be possible to include these variables in the dimensional analysis and thus obtain a more generalized model. If the model parameters for such a model are recognized as standard parameters and are reported by the manufacturer, or are established by a pilot experiment before being applied in any industrial application, this model can then be used very suitably in any practical application to predict flux and rejection, just as other empirical dimensionless equations have become indispensable in many fields of chemical engineering like heat or mass transfer.

NOMENCLATURE

C : solute concentration [kg·m^{-3}], C_b-bulk, C_p-permeate
N : stirrer speed [s^{-1}]
ΔP : pressure differential [Pa]
ρ : density of solution [kg·m^{-3}]
μ : viscosity [Pa·s]
D_s : impeller diameter [m]
t : time [min]
J : volumetric permeate flux [m^3·m^{-2}·s^{-1}]

REFERENCES

Belfort, G. and Nagata, N., "Fluid Mechanics and Cross Flow Filtration: Some Thoughts," *Desalination*, **53**, 57 (1985).
Belfort, G., Davis, R. H. and Zydney, A. L., "The Behavior of Suspen-

sions and Macromolecular Solutions in Cross-low Microfiltration," *J. Membr. Sci.*, **96**, 1 (1994).

Cheryan, M., "Ultrafiltration Handbook," Technomic Publishing Company Inc. (1986).

Goldsmith, R. L., "Macromolecular Ultrafiltration with Macroporous Membranes," *Ind. Eng. Chem. Fundam.*, **10**, 13 (1971).

Iritani, E. and Mukai, Y., "Approach from Physicochemical Aspects in Membrane Filtration," *Korean J. Chem. Eng.*, **14**, 347 (1997).

Jung, C. W. and Kang, L. S., "Application of Combined Coagulation Ultrafiltration Membrane Process for Water Treatment," *Korean J. Chem. Eng.*, **20**, 855 (2003).

Kim, J. P. and Kim, J. J., "Flux Enhancement with Glass Ball Inserted Membrane Module for the Ultrafiltration of Dextran Solution," *Korean J. Chem. Eng.*, **20**, 99 (2003).

Lebrun, R. E., Bonchard, C. R., Rollin, A. L., Masura, T. and Sourirajan, S., "Computer Simulation of Membrane Separation Processes," *Chem. Eng. Sci*., **44**(2), 313 (1989).

Minnikanti, V. S., Dasgupta, S. and De, S., "Prediction of Mass Transfer Coefficient with Suction for Turbulent Flow in Cross Flow Ultrafiltration," *J. Membr. Sci*., **157**, 227 (1999).

Nakao, S., Nomura, T. and Kimura, S., "Characteristics of Macromolecular Gel Layer Formed on Ultrafiltration Tubular Membrane," *AIChE J*., **25**, 615 (1979).

Park, S. J., Yoon, H. H. and Song, S., "Solubilization and Micellar-enhanced Ultrafiltration of o-cresol by Sodium Dodecyl Sulphate Micelles," *Korean J. Chem. Eng.*, **14**, 233 (1997).

Press, W. H., Flannery, P. O., Teukolsky, S. A. and Vettering, W. T., "Numerical Recipes," 2nd Ed., Cambridge University Press, Cambridge (1992).

Redkar, S., Kuberkar, V. and Davis, R. H., "Modeling of Concentration Polarization and Depolarization with High Frequency Back Pulsing," *J. Membr. Sci.*, **121**, 229 (1996).

Ruth, B. F., "Studies in Filtration: Derivation of General Filtration Equations," *Ind. Eng. Chem.*, **27**(6), 708 (1935).

Secchi, A. R., Wada, K. and Tessaro, I. C., "Simulation of an Ultrafiltration Process of Bovine Serum Albumin in Hollow-fiber Membrane," *J. Membr. Sci.*, **160**, 255 (1999).

Shen, J. S. and Probstien, R. F., "On the Prediction of Limiting Flux in Laminar Ultrafiltration of Macromolecular Solution," *Ind. Eng. Chem. Fundam.*, **16**, 459 (1977).

Song, L. and Elimelech, M., "Theory of Concentration Polarization in Cross Flow Filtration," *J. Chem. Soc., Faraday Trans.*, **91**(19), 3389 (1995).

Song, L., "Flux Decline in Crossflow Microfiltration: Mechanisms and Modeling of Membrane Fouling," *J. Membr. Sci.*, **139**, 183 (1998).

Tarleton, E. S. and Wakeman, R. J., "Understanding Flux Decline in Crossflow Microfiltration Part1-Effects of Particles and Pore Size," *Trans. Chem. Eng.*, **71**, 399 (1993).

Trettin, D. R. and Doshi, M. R., "Limiting Flux in Ultrafiltration of Macromolecular Solutions," *Chem. Eng. Commun.*, **4**, 507 (1980).

Trettin, D. R. and Doshi, M. R., "Ultrafiltration in an Unstirred Batch Cell," *Ind. Eng. Chem. Fundam.*, **19**, 189 (1980).

Zeman, L. Z. and Zydney, A L., "Microfiltration and Ultrafiltration," Marcell Dekker Inc. (1996).