

Influence of feed concentration on the accuracy of permeate flux decline prediction in ultrafiltration

M. Cinta Vincent Vela^{a*}, Enrique Bergantiños-Rodríguez^b,
Silvia Álvarez Blanco^a, Jaime Lora García^a

^a*Department of Chemical and Nuclear Engineering, Polytechnic University of Valencia,
C/Camino de Vera s/n, 46022 Valencia, Spain*

Tel. +34 9638 77000, ext. 76381; Fax +34 9638 77639; email: mavinve@iqn.upv.es

^b*Department of Chemical Engineering, Polytechnical Institute José A. Echeverría,
Ave. 114, No. 11901, Havana, Cuba*

Received 14 December 2006; accepted 3 January 2007

Abstract

A theoretical model was used for permeate flux decline prediction. Ultrafiltration experiments were performed varying TMP and feed concentration. The feed solution consisted of an aqueous solution of polyethylene glycol with a molecular weight of 35,000 Da. Monotubular Al₂O₃-TiO₂ ceramic membranes with a molecular weight cut off (MWCO) of 5 kDa (Tami Industries, France) were used in the experiments. Experimental data and model predictions were compared. The influence of feed concentration in the accuracy of permeate flux decline prediction was studied. The model predicted very accurately the reduction in the influence of transmembrane pressure (TMP) on permeate flux as the feed concentration increased. The best predictions were obtained for the highest feed concentration tested. For this feed concentration the influence of TMP on experimental and predicted permeate flux was very low.

Keywords: Permeate flux decline; Concentration; Ultrafiltration; Polyethylene glycol

1. Introduction

A theoretical model that achieves to accurately describe a separation process is a powerful tool for the description, knowledge, prediction, control and optimization of that phenomenon.

Experimental test are not necessary when there is a theoretical model that can provide the same information that can be obtained experimentally. Moreover, theoretical models can help to optimize the value of a variable by managing with the rest of the variables considered by the model. These variables modify the physical or chemical phenomenon described by the model.

*Corresponding author.

Presented at the conference on Desalination and the Environment. Sponsored by the European Desalination Society and Center for Research and Technology Hellas (CERTH), Sani Resort, Halkidiki, Greece, April 22–25, 2007.

Theoretical models are also useful in the optimization of industrial processes, for computer simulation, etc.

Differential equations are the basis of the conservation laws governing the following quantities: energy, mass and linear momentum. They play an important role when modelling physico-chemical processes. Modelling these processes is a challenge due to their complexity as a consequence of the large quantity of variables that have an influence on them and their interrelation. Mathematics is crucial in model formulation and in the development of the required tools for its application.

Advances in the knowledge and modelling of membrane fouling processes have been remarkable in the past fifteen years. Fouling is responsible for permeate flux decline in microfiltration and ultrafiltration processes. However, the main fouling mechanisms, the variables affecting fouling and their interrelation are a field with high expectations and not enough results.

Membrane literature is full of articles concerning fouling mechanisms that propose theoretical and empirical models to describe the relation between permeate flux and other variables: transmembrane pressure (TMP), crossflow velocity, feed concentration, particle size, etc.

The first models proposed for the prediction of permeate flux decline with time and for the prediction of the achievement of steady-state were obtained by means of the classic filtration theory. Pore blocking and cake formation models were used to describe this process. However they do not account for the effect of the tangential flow. Therefore, these models predict a final permeate flux value of zero, which does not occur in membrane crossflow filtration.

Several models accounting for the dynamic nature of the fouling process were developed later: a model that applies the dead-end ultrafiltration theory in the dynamic case [2], Song and Elimelech's dynamic model for crossflow ultrafiltration (this model has been used and modified

in many occasions [1,3–7]), Bhattacharjee and Bhattacharya's model for osmotic pressure controlled and gel layer controlled ultrafiltration [8], dynamic model that combines pore blocking and gel layer formation [9], dynamic model for gel layer formation [10].

These models were used by Vincent et al. [11–16] in the ultrafiltration of PEG with ceramic membranes. The research carried out by Song et al. constitutes an important progress in the knowledge and modelling of microfiltration and ultrafiltration fouling processes. The model proposed focus on concentration polarisation and gel layer formation. It also takes into account the concept of critical pressure and its relation with gel layer formation. It can be considered as the second part of the research carried out by Wakeman [17] about cake layer formation and growth over the membrane surface distinguishing different regions.

As in most of the proposed dynamic models, some parameters must be experimentally or theoretically determined. However the most commonly used equations for this purpose are not very accurate, for example equations for gel layer concentration, C_g , and intrinsic resistance, r_c , determination.

This work focuses on Song and Elimelech's dynamic model because it is considered to be the most integral and versatile model.

2. Materials and methods

The experiments were carried out in the ultrafiltration pilot plant described elsewhere [11–12,14]. Fouling experiments were performed with monotubular membranes. Their active layer consisted of $\text{TiO}_2/\text{Al}_2\text{O}_3$ and they were manufactured by Tami Industries, France. They were 20 cm long with an external and internal diameter of 10 and 6 mm, respectively. The membrane area was 35.25 cm² and its molecular weight cut-off was 5 kDa.

A total amount of 36 experiments were carried out with the Tami membrane. In these experiments transmembrane pressure (0.2, 0.3, 0.4 and 0.5 MPa), feed concentration (5, 10 and 15 g/L) and crossflow velocity (1, 2 and 3 m/s) were varied. The temperature was set at 25°C. Aqueous solutions of polyethylene glycol (PEG) of 35 kDa molecular weight were used as feed.

All the experiments were carried out with a constant feed concentration. For that purpose retentate and permeate were recycled back to the feed tank. The same membrane was used for all the experiments. After each experiment the membrane was cleaned at 40°C with a 0.25 g/L NaClO aqueous solution at pH 11 by adding NaOH to prevent steel corrosion. Samples of feed and permeate were taken in each experiment to determine COD and therefore estimate membrane retention of the solute vs. time.

Finally, eight experiments were repeated to validate the accuracy of the experimental methodology.

2.1. Modelling

Song and Elimelech [1] formulated a theory based in novel aspects of crossflow ultrafiltration. This theory contributed to a better understanding of the process involved in the bounding layer formation and in the gel layer growth and formation. It also proposed a mathematical model to describe the transition from the initial non-steady state of the ultrafiltration process to the final steady-state achieved when the thickness of the gel layer remains constant all over the membrane surface. This theory was checked in the ultrafiltration of colloids [1].

The model considers a gradual formation of the gel layer differentiating two regions over the membrane surface: the region near the feed solution inlet where the gel layer is rapidly formed and steady-state is instantly reached and a second region where steady-state is slowly reached. There is a frontier between the steady-state and

the non-steady state region that moves along the membrane.

Song and Elimelech [1] formulated an adimensional parameter valid for spherical particles; the critical filtration number (Eq. (1)):

$$N_F = \frac{4\pi a_p^3}{3kT} \Delta P_c \quad (1)$$

where a_p is the particle radius, k Boltzmann's constant, T is temperature and ΔP_c is the pressure loss due to the concentration polarisation layer.

The pressure loss in the concentration polarisation layer achieves a maximum critical value, ΔP_{cc} . Above this critical value, also named critical pressure, the gel layer begins to form. The filtration number in Eq. (1) that corresponds to the critical pressure is named critical filtration number, N_{FC} . Below the critical pressure, a concentration polarisation layer forms over the membrane surface. This layer has a maximum concentration below the gel layer concentration, C_g . Above the critical pressure, the maximum concentration near the membrane surface is C_g and the gel layer begins to form.

The critical filtration number is defined [4] as follows:

$$N_{FC} = \int_0^{\theta_{GV}} \frac{1 + \frac{2}{3}\theta^5}{1 - \frac{3}{2}\theta + \frac{3}{2}\theta^5 - \theta^6} 3\theta^2 d\theta \quad (2)$$

where $\theta = C_v^{1/3}$, C_v being concentration (v/v). In order to estimate the critical filtration number, an estimation of the gel layer concentration, C_{GV} , is required.

The critical filtration number relates the energy needed for the transportation of a molecule from the bulk solution towards the membrane surface with the kinetic energy of the molecule. As the critical filtration number increases, the energy needed for the transportation of a molecule towards the membrane surface also increases.

The parameter ΔP_{cc} is estimated by means of Eq. (1), after estimating the critical filtration number using Eq. (2).

The time, t_{est} , at which steady-state is achieved for ultrafiltration processes controlled by the gel layer resistance can be estimated by means of Eq. (3) [6]. At t_{est} , the gel layer thickness and the permeate flux remain constant with time.

$$t_{est} = 0.351 \left(\frac{L}{D^2 \gamma} \right)^{\frac{2}{3}} \left(\frac{C_g}{C_o} \right)^{\frac{1}{3}} \left(\frac{\Delta P - \Delta P_c}{r_c} \right) \quad (3)$$

In Eq. (3), L is the membrane length, D is the diffusion coefficient of the solute, C_g and C_o are the concentration in the gel layer and in the feed, respectively, ΔP is the transmembrane pressure, r_c is the intrinsic resistance of the gel layer and γ is the shear rate.

The specific resistance of the gel layer is given by the Kozeny-Carman equation (Eq. (4)) for the flow across a porous media.

$$r_c = \frac{45\mu(1 - \varepsilon)^2}{a_p^2 \varepsilon^3} \quad (4)$$

where μ is the dynamic viscosity of the permeate, $\varepsilon = (1 - C_{GV})$ is the cake layer porosity and a_p is the radius of the solute molecule.

For $t < t_{est}$, permeate flux in the non-equilibrium region, $J(t)$, can be expressed as follows:

$$J(t) = \frac{(\Delta P - \Delta P_c)}{\mu R_m} \left[1 + \frac{2r_c (\Delta P - \Delta P_c) C_o}{\mu^2 R_m^2 C_g} t \right]^{\frac{1}{2}} \quad (5)$$

The frontier location, $x(t)$, between the equilibrium region and the non-equilibrium region is given by Eq. (6):

$$x(t) = 4.81 (D^2 \gamma) \left(\frac{C_o}{C_g} \right)^{\frac{1}{2}} \left(\frac{r_c}{\Delta P - \Delta P_c} t \right)^{\frac{3}{2}} \quad (6)$$

When $t < t_{est}$, the mean permeate flux along the membrane, $J_m(t)$, is

$$J_m(t) = \frac{1.31}{L} \left[\frac{C_g D^2 \gamma}{C_o} x(t)^2 \right]^{\frac{1}{3}} + \frac{L - x(t)}{L} J(t) \quad (7)$$

When $t > t_{est}$, then $x(t) = L$, and the limiting permeate flux, J_{lim} , is achieved. The limiting permeate flux is independent of the transmembrane pressure (Eq. (8)).

$$J_{lim} = 1.31 \left[\frac{C_g D^2 \gamma}{C_o L} \right]^{\frac{1}{3}} \quad (8)$$

3. Results and discussion

Due to the small values of gel layer concentration obtained, the values of ΔP_{cc} estimated are low when compared with the TMP. For the same reason, osmotic pressure is also negligible.

In Figs. 1–3, the experimental results for permeate flux decline are compared with those predicted by the model for a crossflow velocity of 1 m/s. For this crossflow velocity the probability of cake layer formation is very high.

The differences observed between experimental results and those predicted by the model are similar to those obtained by Vincent et al. [12]. These differences are noticeable for short time scales, for which predicted permeate flux is higher than that experimentally observed. Presumably, a fouling mechanism not considered by the model is taking part at the beginning of ultrafiltration experiments.

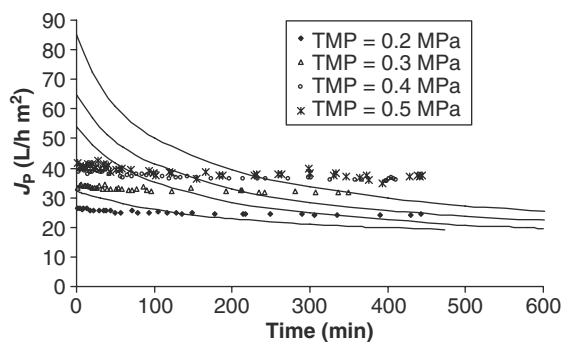


Fig. 1. Comparison between experimental data and model predictions for a crossflow velocity of 1 m/s and a feed concentration of 5 g/L.

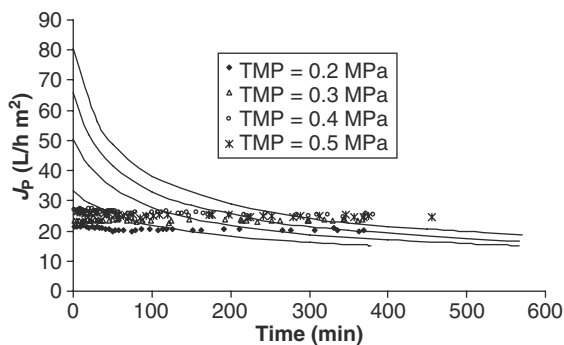


Fig. 2. Comparison between experimental data and model predictions for a crossflow velocity of 1 m/s and a feed concentration of 10 g/L.

In Fig. 1 it can be observed that experimental results and those predicted by the model are more similar for low TMPs (0.2 MPa). In all cases, the model predictions for steady-state permeate flux are inferior to the steady-state values obtained experimentally. Furthermore, the model predicts a time-delayed achievement of steady-state permeate flux when compared with the experimental results. This can be explained considering that, although the model explains ultrafiltration supposing that steady-state permeate flux is achieved by the growth and consolidation of the gel layer, this may not be correct for all the experimental conditions tested.

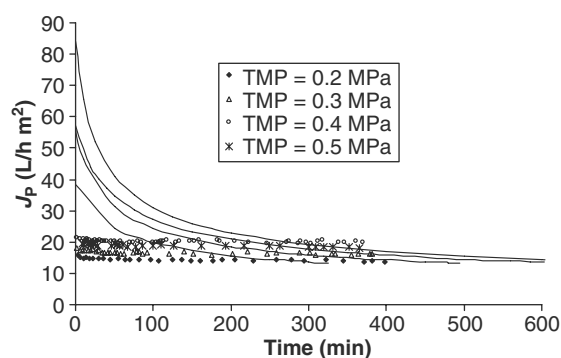


Fig. 3. Comparison between experimental data and model predictions for a crossflow velocity of 1 m/s and a feed concentration of 15 g/L.

For a feed concentration of 10 g/L, a similar performance is observed (Fig. 2). Nevertheless, the model predicts a relatively low diminution of permeate flux with time only for a TMP of 0.2 MPa. Therefore, the time needed for steady-state to be achieved predicted by the model is in accordance with the experimental results for this TMP.

When the feed concentration is 15 g/L (Fig. 3), the experimental results and those predicted by the model are to some extent similar only when more than four hours from the beginning of the ultrafiltration experiment have passed. Besides, predicted steady-state permeate flux is quite similar to the experimental one.

Experimental and predicted permeate flux are closer for the lowest feed concentration (5 g/L) and the lowest TMP (0.2 MPa) tested. The value of the initial permeate flux estimated by the model is near to the experimental results for these experimental conditions. This results in a lower permeate flux decline. When the more diluted feed solution is exposed to the lowest TMP, initial permeate flux is also the lowest. Consequently, the pore blocking fouling of the membrane, which causes a rapid initial flux decline, diminishes.

For the minimum feed concentration tested (5 g/L), differences between experimental and predicted initial permeate flux are the lowest. These differences increase when the concentration near the membrane surface increases.

The time required to achieve steady-state diminishes with an increment in feed concentration and augments when increasing TMP, as predicted by the model (Eq. (3)). The thickness of the gel layer rises as TMP increases. As a result, more solute molecules accumulate in the gel layer due to the convective transport because steady-state permeate flux remains constant. The intrinsic resistance of the gel layer does not vary with TMP.

As feed concentration and TMP increase, the difference between the predicted initial permeate flux and that obtained experimentally increases significantly. This suggests that a fouling

mechanism not considered by the model takes place for short time scales. This fouling mechanism is more severe as feed concentration and TMP increase, what can be related to an instantaneous adsorption of molecules and/or pore blocking and never to a high concentration polarisation resistance, as gel concentration values estimated are low.

4. Conclusions

The main conclusions of this work are

- As membrane resistance is high and the values of the gel layer concentration estimated are low, membrane resistance and an instantaneous pore blocking and/or adsorption phenomenon control ultrafiltration of PEG 35,000 for the experimental conditions tested. As a result, for most of the experimental conditions tested, gel layer formation was not enhanced. Therefore, permeate flux varied slightly with time. According to the values of the critical pressure obtained, a gel layer forms over the membrane surface. The concentration of the gel layer is low and it is far from the solubility limit of PEG. Consequently, the gel layer resistance is also low and it scarcely contributes to permeate flux decline. The gel layer thickness is small mainly due to a reduced TMP excess available for its formation. A reduced membrane length also contributes to a rapid achievement of steady-state permeate flux.
- For the experimental conditions tested, the limiting permeate flux as well as the maximum gel layer thickness is only accomplished for TMPs of 0.4 and 0.5 MPa.
- The variation of permeate flux with TMP decreases with an increase in the feed concentration. At high feed concentrations this variation is negligible.
- For low TMPs (0.2 and 0.3 MPa) the influence of feed concentration on permeate fluxes is lower than in the case of high TMPs (0.4 and 0.5 MPa).

- The discrepancies between the model analysed and the experimental results are due to the following facts:
 - The model does not consider a rapid initial permeate flux decline phenomenon caused by adsorption or pore blocking. This phenomenon may be occurring at the highest TMPs set in the experiments.
 - The model is very sensitive to the gel layer concentration values. The equations available to estimate de gel layer concentration are not very precise. Therefore the applicability of this model and others is limited.

Acknowledgements

The authors of this work wish to gratefully acknowledge the financial support of the Spanish Ministry of Science and Technology (MCYT) through its project no. CTQ2005-03398.

References

- [1] L. Song and M. Elimelech, Theory of concentration polarization in cross-flow filtration, *J. Chem. Soc., Faraday Trans.*, 91 (1995) 3389–3398.
- [2] R.H. Davis, Modeling of fouling of crossflow microfiltration membranes, *Separation Purification Methods*, 21 (1992) 75–126.
- [3] L. Song, Flux decline in cross-flow microfiltration and ultrafiltration: mechanisms and modelling of membrane fouling, *J. Membr. Sci.*, 139 (1998) 183–200.
- [4] L. Song, A new model for the calculation of the limiting flux in ultrafiltration, *J. Membr. Sci.*, 144 (1998) 173–185.
- [5] L. Wang and L. Song, Flux decline in cross-flow microfiltration and ultrafiltration: experimental verification of fouling dynamics, *J. Membr. Sci.*, 160 (1999) 41–45.
- [6] M. Zhang and L. Song, Mechanisms and parameters affecting flux decline in cross-flow microfiltration and ultrafiltration of colloids, *Environ. Sci. Technol.*, 34 (2000) 3767–3773.
- [7] M. Zhang and L. Song, Pressure-dependent permeate flux in ultra and microfiltration, *J. Environ. Eng.*, 126 (2000) 667–674.

- [8] P.K. Bhattacharya and S. Bhattacharjee, Flux decline behaviour with low molecular weight solutes during ultrafiltration in an unstirred batch cell, *J. Membr. Sci.*, 72 (1992) 149–161.
- [9] C.C. Ho and A.L. Zydney, A combined pore blockage and cake filtration model for protein fouling during microfiltration, *J. Coll. Interf. Sci.*, 232 (2000) 389–399.
- [10] N. Mugnier, J.A. Howell and M. Ruf, Optimisation of a back-flush sequence for zeolite microfiltration, *J. Membr. Sci.*, 175 (2000) 149–161.
- [11] M.C. Vincent Vela, S. Álvarez-Blanco and J. Lora-García, Crossflow ultrafiltration of cake forming solutes: a non-steady state model, *Desalination*, 184 (2005) 347–356.
- [12] M.C. Vincent Vela, S. Álvarez-Blanco, J. Lora-García and E. Bergantiños-Rodríguez, Prediction of flux decline in the ultrafiltration of macromolecules, *Desalination*, 192 (2006) 323–329.
- [13] M.C. Vincent Vela, S. Álvarez-Blanco, J. Lora-García and E. Bergantiños-Rodríguez, Application of a dynamic model that combines pore blocking and cake formation in crossflow ultrafiltration, *Desalination*, 200 (2006) 138–139.
- [14] M.C. Vincent Vela, S. Álvarez-Blanco, J. Lora-García and E. Bergantiños-Rodríguez, Application of a dynamic model for predicting flux decline in crossflow ultrafiltration, *Desalination*, 198 (2006) 303–309.
- [15] M.C. Vincent Vela, S. Álvarez-Blanco, J. Lora-García, J.M. Gozávez-Zafrilla and E. Bergantiños-Rodríguez, Modelling of flux decline in crossflow ultrafiltration of macromolecules: comparison between predicted and experimental results, *Desalination*, 204 (2007) 328–334.
- [16] M.C. Vincent Vela, S. Álvarez-Blanco, J. Lora-García, J.M. Gozávez-Zafrilla and E. Bergantiños-Rodríguez, Utilization of a shear induced diffusion model to predict permeate flux in the crossflow ultrafiltration of macromolecules, *Desalination*, 206 (2007) 61–68.
- [17] R.J. Wakeman, Visualisation of cake formation in crossflow microfiltration, *Trans. ICHemE.*, 72 (1994) 530–540.