

Modelling of flux decline in crossflow ultrafiltration of macromolecules: comparison between predicted and experimental results

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

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

Tel: +34 963 877000 Ext: 76383; Fax: +34 963 877639; email: mavinve@iqn.upv.es

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

Received 29 January 2006; Accepted 12 February 2006

Abstract

The purpose of this work was to compare the experimental results on flux decline with time in the ultrafiltration of macromolecules with the results predicted by a model based in the resistance in series model. The model considers the osmotic pressure, gel-layer formation and adsorption as responsible for flux decline. In this paper, the change in permeate flux with time was predicted theoretically, without the use of any empirical data. A ceramic ZrO₂-TiO₂ monotubular Carbosep M2 membrane (Orelis, S.A., France) with a molecular weight cut-off of 15 kDa was selected to perform the experiments. Aqueous solutions of PEG 35000 were used as feed. The experimental results obtained at different flow rates and transmembrane pressures (TMPs) were compared with the theoretical predictions. The best predictions were obtained for low crossflow velocities (1 m/s), especially for long time scales. However, for long time scales permeate flux was under predicted for high crossflow velocities (2 and 3 m/s). The reason for these results may be found in the increased possibilities of gel layer formation at low crossflow velocities.

Keywords: Crossflow ultrafiltration; Modelling; Flux decline; Macromolecules

*Corresponding author.

Presented at EuroMed 2006 conference on Desalination Strategies in South Mediterranean Countries: Cooperation between Mediterranean Countries of Europe and the Southern Rim of the Mediterranean. Sponsored by the European Desalination Society and the University of Montpellier II, Montpellier, France, 21-25 May 2006

1. Introduction

Ultrafiltration (UF) has been widely used for the separation of macromolecules and colloidal particles from liquids [1]. Membrane fouling is inherent to the ultrafiltration process and it causes permeate flux decline with time as the retained solutes accumulate on the membrane surface and within the pores [2]. Fouling of the membrane decreases the productivity, increases the costs and makes membrane processes less competitive [3]. Therefore, being able to predict flux decline with time under various conditions is of great interest for process design and optimization to successfully select the operating conditions that minimize flux decline with time. Nowadays, flux data are obtained from time consuming pilot tests. A model able to predict permeate flux under any operating condition is very interesting to substitute the pilot tests.

A number of models have been developed to explain the fouling mechanisms of membrane processes [4]. However, most of these models are empirical or semi-empirical [5]. These models have the advantage of being very accurate, but they need experimental data to be used.

In this work, UF experiments were performed and the results obtained at different operating conditions were compared with the theoretical predictions. The similarities and differences between experimental and predicted results were analysed on the basis of the hypothesis considered in the model. All the model parameters were theoretically calculated, without the use of empirical data.

2. Theoretical analysis

A model [6] based in the resistance in series model was considered. This model integrates in the same analytical expression the osmotic pressure as well as gel layer formation as responsible for flux decline with time.

It also accounts for the contribution of adsorption to fouling. The main equation proposed by this model is Eq. 1. The first term in the model equation includes the influence of the osmotic pressure and adsorption on flux decline, while the second term considers the cake formation phenomenon.

$$J_P = \left(\frac{[\mu \cdot (R_m + R_a + R_{osm})]^2}{\Delta P^2} + \frac{2 \cdot a \cdot C_0 \cdot \mu \cdot t}{\Delta P} \right)^{-\frac{1}{2}} \quad (1)$$

In Eq. 1 J_P is the permeate flux, ΔP is the transmembrane pressure, μ is the dynamic viscosity of the permeate, R_m is the membrane hydraulic resistance, R_a is the adsorption resistance, R_{osm} is the osmotic resistance, a is the specific resistance of the gel layer, C_0 is the feed concentration and t is time.

The model considers that gel layer concentration is independent of the applied transmembrane pressure and once the solute adsorption equilibrium is achieved the adsorption resistance remains constant.

The specific resistance of the cake layer is given by Eq. 2 [7].

$$a = 45 \cdot \frac{(1 - \varepsilon)}{\varepsilon^3 \cdot a_p^2 \cdot \rho_g}, \text{ being } \varepsilon = 1 - C_{gv} \quad (2)$$

where ε is the cake porosity, a_p is the radius of the solute molecule, ρ_g is the density of the gel layer and C_{gv} is the gel layer concentration. All the parameters in Eq. 2 were calculated as explained in previous papers [8].

The contribution of the osmotic resistance was calculated using Flory's equation as recommended in the literature [9–14]. The contribution of the adsorption resistance was estimated from previous data on PEG adsorption on ZrO_2 and TiO_2 surfaces [15,16].

In the literature, when this model was used, the model parameters were empirically

estimated from the experimental results. In this paper every model parameter was theoretically calculated without using experimental data.

3. Materials and methods

3.1. Materials

A Carbosep M2 monotubular ZrO_2-TiO_2 ceramic membrane with a molecular weight cut off (MWCO) of 15 kg/mol was used. The membrane was supplied by Orelis, S.A. (France). It had a pore diameter of 4 nm, an internal diameter of 6 mm and an active surface area of 35.5 cm^2 .

UF fouling experiments were performed with aqueous solutions of polyethylene glycol (PEG). PEG flakes with a molecular weight (MW) of 35000 g/mol were obtained from Merck-Schuchardt (Germany) Solutions of 5 g/L were prepared with deionized water.

Cleaning of the membrane was performed with aqueous solutions of NaOH in pellets or flakes supplied by Panreac (Spain).

3.2. Experimental set up

A Crossflow UF device (Fig. 1) was specially designed and fabricated for this research at the Polytechnic University of Valencia. It consisted of two circuits: one for the circulation of the feed solution and the other one for the circulation of the cleaning solution. To maintain a constant concentration in the feed tank, both the permeate and the retentate were recycled back to the feed tank. Moreover, due to the small membrane area and the large volume of the feed tank, the quantity of PEG deposited on the membrane was minimal compared to the total amount of PEG in the feed tank and it will not alter the feed tank concentration.

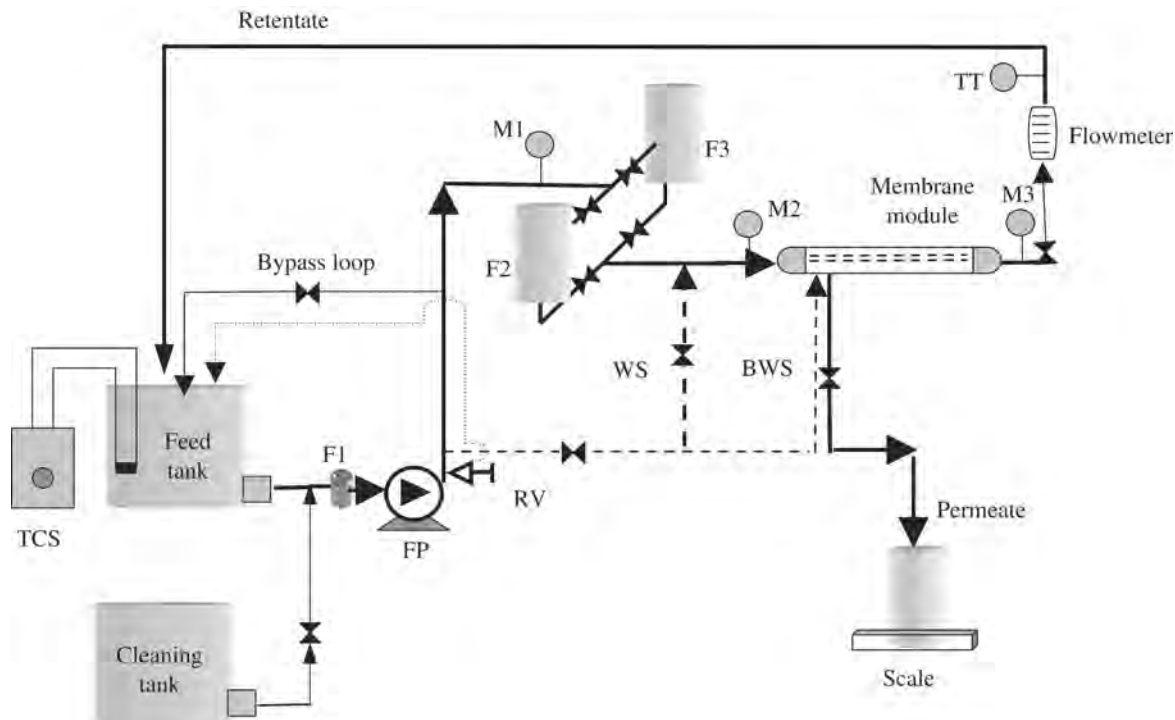


Fig. 1. Schematic diagram of the UF pilot plant used in the experiments.

The pilot plant was also equipped with a washing and a backwashing system and a temperature control system. The feed solution was fed to the membrane module by a variable speed pump, thus allowing a range of crossflow velocities to be tested.

3.3. Experimental procedure

The experiments were designed to study flux decline with time in crossflow ultrafiltration under different experimental conditions and to compare the results with the data predicted by the model for those operating conditions. The experiments were performed at different feed flow rates and transmembrane pressures (TMPs). The flow rate was varied between 1 and 3 m/s and the TMP between 0.1 and 0.4 MPa. All the runs were carried out at a temperature of 25°C.

The water permeability of the membrane at 25°C was determined with deionized water.

The feed solution was prepared by dissolving PEG in deionized water until a concentration of 5 g/L was achieved. The feed solution was not allowed to pass through

the membrane until the temperature was stabilized at a value of 25°C. The pilot plant was stopped after 7 h of operation, time enough to reach quasi steady-state conditions.

The same membrane was used for all the experiments. The membrane was cleaned after each fouling experiment. First the membrane was rinsed with deionized water, then it was cleaned with an aqueous NaOH solution of 0.2% w/w at 50°C and finally it was rinsed again with deionized water. Once the cleaning process was finished, the water permeability of the membrane was measured. The initial permeability of the membrane was completely recovered after the cleaning cycle.

4. Results and discussion

Experimental data on pure water permeate flux were used to evaluate the membrane hydraulic resistance. The value of the membrane resistance obtained was $6.897 \cdot 10^{12} \text{ m}^{-1}$.

The data estimated by the model were compared with the experimental results in Figs. 2–4. In Fig. 2, model predictions were compared with experimental data for a cross-

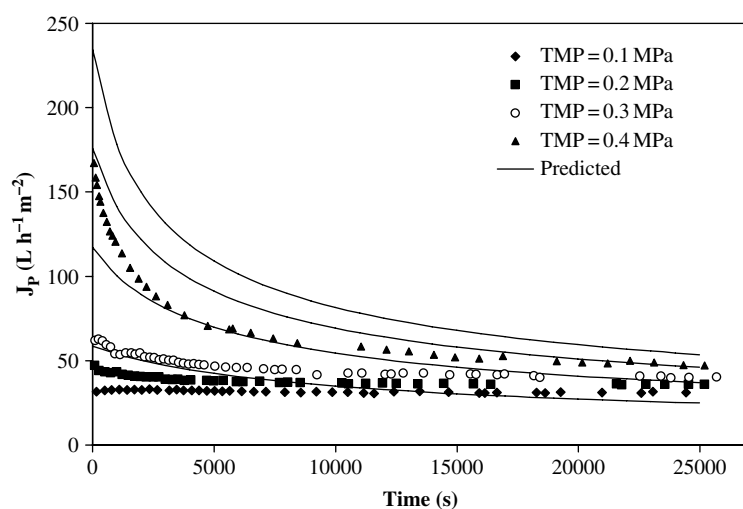


Fig. 2. Comparison between experimental results and permeate flux predicted by the model at a crossflow velocity of 1 m/s.

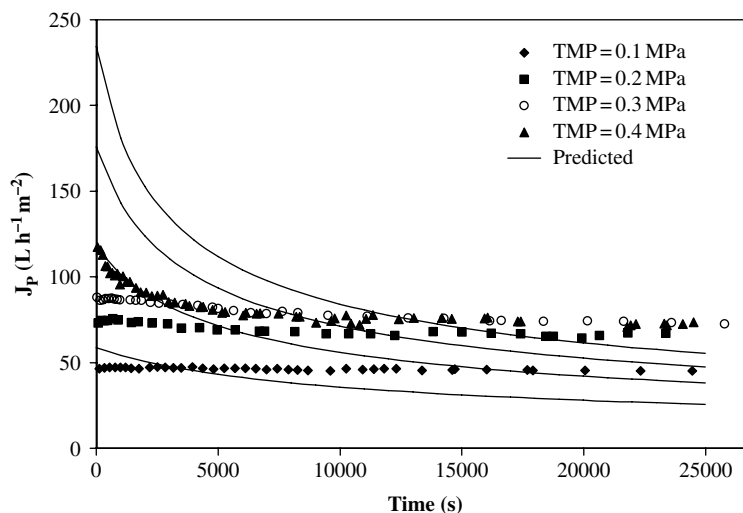


Fig. 3. Comparison between experimental results and permeate flux predicted by the model at a crossflow velocity of 2 m/s.

flow velocity of 1 m/s and four different TMPs. The symbols correspond to the experimental results on permeate flux vs. time and the continuous lines correspond to the values calculated by the model. For long time scales, predicted permeate fluxes were in accordance with experimental results. The shape of the predicted curve was also similar to the experimental results. However, for short time scales permeate flux was over predicted.

Fig. 3 compares model predictions with experimental data for a crossflow velocity of 2 m/s and four different TMPs. Even for long time scales, the predictions were not in agreement with the experimental results. For long time scales predicted permeate fluxes were lower than experimental ones. However, for short time scales permeate flux was again over-predicted. In this case, the discrepancies between predicted and experimental data were greater than those observed for 1 m/s. The shape of the predicted flux decline curve differed more from the experimental results than that obtained at lower crossflow velocities. Considering that at high crossflow

velocities, gel layer formation can be negligible [17], flux decline could be due to concentration polarization as well as adsorption. Pore blocking was unlikely to be the cause of fouling as no rapid initial flux decline was observed under these experimental conditions. Therefore, the reason for the discrepancies between experimental and predicted results could be that the model analysed is not suitable when the gel layer does not form.

In Fig. 4, model predictions were compared with experimental data for a cross flow velocity of 3 m/s. the discrepancies between predicted and experimental results for all time scales were even greater than those observed for a crossflow velocity of 2 m/s. The differences in the shape of the curve for flux decline predicted by the model and the experimentally observed one were also greater than those obtained for a crossflow velocity of 2 m/s. For a crossflow velocity of 3 m/s, the permeate flux decline with time experimentally observed was minimal. However, the model predicted a noticeable permeate flux decline. The model considers

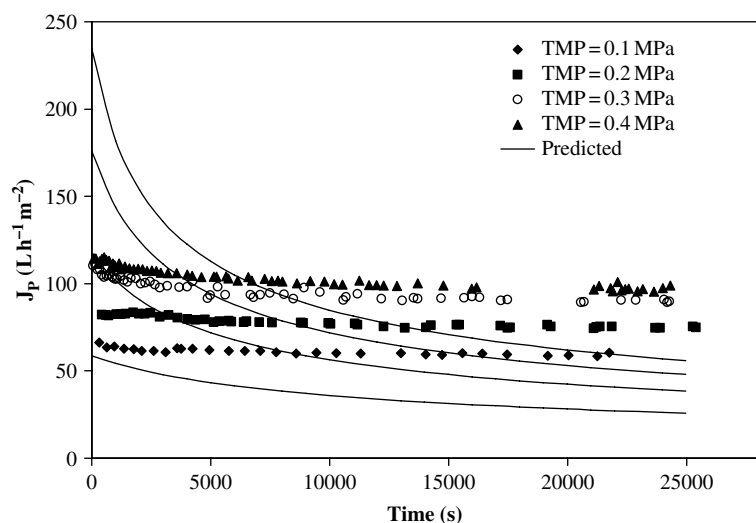


Fig. 4. Comparison between experimental results and permeate flux predicted by the model at a crossflow velocity of 3 m/s.

severe membrane fouling due to gel layer formation, although gel layer formation may not occur at high crossflow velocities. This can be reason for the discrepancy between experimental and predicted results at high crossflow velocities.

For all the crossflow velocities, as TMP increases, the difference between the permeate fluxes predicted by the model at different TMPs was reduced. As TMP increases, the process moves from a pressure controlled region to a mass transfer controlled region. This change was also predicted by the model.

5. Conclusions

The best predictions were obtained for low crossflow velocities (1 m/s), specially for long time scales. Moreover, the shape of the curve for predicted permeate flux vs. time was closer to the experimental results for low crossflow velocities. The model considers gel formation as the main fouling mechanism. Gel layer is more likely to be formed at low crossflow velocities. This can be the reason why the best agreement between experimental

and predicted results was observed at 1 m/s. For short time scales permeate flux was over predicted in all cases, being more noticeable for high crossflow velocities. For long time scales permeate flux was under predicted for high crossflow velocities (2 and 3 m/s).

Symbols

- a — specific resistance of the cake layer (m/kg)
- a_p — radius of the PEG molecule (m)
- C_{gv} — gel layer concentration (v/v)
- C_0 — feed concentration (kg/m³)
- J_P — permeate flux (m/s)
- ΔP — transmembrane pressure (Pa)
- R_a — adsorption resistance (m⁻¹)
- R_{osm} — osmotic resistance (m⁻¹)
- R_m — membrane hydraulic resistance (m⁻¹)
- t — time (s)

Greek symbols

- ε — cake porosity (dimensionless)
- μ — dynamic viscosity (kg/m/s)
- ρ_g — density of the gel layer (kg/m³)

Abbreviations

MW	—	molecular weight
MWCO	—	molecular weight cut off
PEG	—	polyethylene glycol
TMP	—	transmembrane pressure
UF	—	ultrafiltration

References

- [1] L. Song, A new model for the prediction of the limiting flux in ultrafiltration, *J. Membr. Sci.*, 144 (1998) 173–185.
- [2] L. Wang and L. Song, Flux decline in crossflow microfiltration and ultrafiltration: experimental verification of fouling dynamics, *J. Membr. Sci.*, 160 (1999) 41–50.
- [3] B. Tansel, W. Y. Bao and I. N. Tansel, Characterization of fouling kinetics in ultrafiltration systems by resistances in series model *Desalination*, 129 (2000) 7–14.
- [4] E. Iritani, Y. Mukai and E. Hagihara, Measurements and evaluation of concentration distributions in filter cake formed in dead-end ultrafiltration of protein solutions, *Chem. Eng. Sci.*, 57 (2002) 53–62.
- [5] V. Gekas, P. Aimar, J.-P. Lafaille and V. Sánchez, A simulation study of the adsorption-concentration polarisation interplay in protein ultrafiltration, *Chem. Eng. Sci.*, 48 (1993) 2753–2765.
- [6] S. Bhattacharjee and P.K. Bhattacharya, Flux decline behaviour with low molecular weight solutes during ultrafiltration in an unstirred batch cell, *J. Membr. Sci.*, 72 (1992) 149–161.
- [7] S. De and P.K. Bhattacharya, Modeling of ultrafiltration process for a two-component aqueous solution of low and high (gel-forming) molecular weight solutes, *J. Membr. Sci.*, 136 (1997) 57–69.
- [8] M.C.V. Vela, S.Á. Blanco and J.L. García, Crossflow ultrafiltration of cake forming solutes: a non-steady state model *Desalination*, 184 (2005) 347–356.
- [9] S. Jacob and M.Y. Jaffrin, Purification of brown cane sugar solutions by ultrafiltration with ceramic membranes: investigation of membrane fouling, *Sep. Sci. Technol.*, 35 (2000) 989–1010.
- [10] C.S. Parnham and R.H. Davis, Protein recovery from bacterial cell debris using crossflow microfiltration with backpulsing, *J. Membr. Sci.*, 118 (1996) 259–268.
- [11] S. Bhattacharjee, and P.K. Bhattacharya, Prediction of limiting flux in ultrafiltration of kraft black liquor, *J. Membr. Sci.*, 72 (1992) 137–147.
- [12] S. De and P.K. Bhattacharya, “Flux prediction of black liquor in crossflow ultrafiltration using low and high rejecting membranes”, *J. Membr. Sci.*, 109 (1996) 109–123.
- [13] S. Ghose, A. Poddar, S. Datta and C. Battacharjee, Numerical simulation of an unstirred batch ultrafiltration process based on the boundary layer concept, *Sep. Purific. Technol.*, 16 (1999) 75–81.
- [14] A. Poddar, C. Bhattacharjee and S. Datta, Simulation of unstirred batch ultrafiltration system based on analytical solution of boundary layer equation, *Sep. Sci. Technol.*, 34 (1999) 2485–2500.
- [15] Y.W. Zhang, M. Tang, X. Jin, C.S. Liao and C.H. Yan, Polymeric adsorption behaviour of nanoparticulate yttria stabilized zirconia and the deposition of as-formed suspensions on dense α -Al₂O₃ substrates *Solid State, Sci.*, 5 (2003) 435–440.
- [16] T. Hamieh, B. Siffert and A. MPandou, Thickness of non-ionic polymer layers carried by inorganic adsorbents in the case of the TiO₂-poly ethylenglycol system, *Adv. Powder Technol.*, 11 (2000) 271–277.
- [17] R.H. Davis, Modeling of fouling of crossflow microfiltration membranes, *Sep. Purific. Methods*, 21 (1992) 75–126.