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Estimation of the gel layer concentration in ultrafiltration: Comparison of different methods

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ABSTRACT

Fouling is one of the major limitations of membrane applications. Gel layer formation is a common fouling mechanism that increases the membrane fouling resistance. In this work the estimation of the gel layer concentration was performed from experimental values obtained in several ultrafiltration experiments using three methods: the gel-polarization model, the mechanistic model for gel layer formation proposed by Song and an expression of the concentration polarization modulus developed for tubular membranes and turbulent flow. The results were compared and analyzed. Two types of monotubular ceramic membranes with different MWCO (5 and 15 KDa) were used in the experiments. Polyethylene glycol (PEG) of 35,000 Da in distilled water was used as feed. The experiments were performed at different feed flow rates (1–3 m/s), transmembrane pressures (0.1–0.5 MPa), temperatures (15–40°C) and constant feed concentrations (5–15 g/L). Values of the gel layer concentration estimated with the gel-polarization model differed significantly from the ones estimated using the other two methods previously mentioned. Therefore, the gel-polarization model was less suitable for the gel layer concentration estimation than the others.

Keywords: Model; Ultrafiltration; Gel layer

1. Introduction

In ultrafiltration (UF), the formation of a gel layer between the concentration polarization layer and the membrane surface occurs when the accumulation of molecules near the membrane surface achieves a maximum concentration value. Once the gel layer begins to form, molecules arriving to the gel layer contribute to increase the gel layer thickness until steady state is achieved. The steady state is attained when the convective flow of molecules towards the membrane surface is compensated with the diffusive transport from the high concentration region of the feed solution towards the bulk solution. This diffusive transport is enhanced by the tangential flow. The thickness of the layer depends on operational parameters such as transmembrane pressure (TMP), crossflow velocity (CFv) and temperature. It also depends on the properties of the feed solution: feed concentration, solute diffusivity, etc. The gel layer increases the membrane fouling resistance.

Field et al. [1] related the formation of the gel layer to the concept of critical flux. They defined the critical flux as

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the value of the permeate flux from which the gel layer begins to form. They also defined the critical pressure as the minimum pressure value required for the formation of the gel layer.

On the other hand, Song and Elimelech [2] proposed a relationship between the critical pressure and the critical filtration number. The critical filtration number was estimated from the values of the gel layer concentration. The critical pressure was considered in a well-known model for the prediction of permeate flux in crossflow UF [3]. Some of the experiments shown in this paper were compared with theoretical predictions of the afore-mentioned model [4].

The critical flux depends on the hydrodynamic properties of the UF system and also on thermodynamic properties and solvent–solute interactions. Some authors [5,6] reported two types of critical flux: the strong form (up to critical flux, flux is identical to clean water flux) and the weak form (up to critical flux, flux is proportional to TMP with no hysteresis observed in flux vs. TMP curves with any increases or decreases in flux). More studies related to critical flux are found in the literature [7–10]. It must be noticed that some of the experiments shown in this paper may be near the critical flux since very low permeate flux decline with time occurred in some cases.

2. Materials and methods

2.1. Membranes

Two types of monotubular ceramic membranes were used in the experiments: Carbosep M2 ZrO_2-TiO_2 membranes supplied by Orelis (France) with a molecular weight cut-off (MWCO) of 15 KDa and TiO_2-Al_2O_3 Tami MSKT membranes supplied by Tami (France) with a MWCO of 5 KDa. The area of both membranes was 35.5 cm^2; they were 20 cm long and they had an internal diameter of 6 mm.

2.2. Fouling experiments

It has been reported that polyethylene glycol (PEG) can form a gel layer during UF [11–13]. Moreover, PEG UF processes have been modelled on many occasions with UF models that consider the formation of a gel layer over the membrane surface [14,15]. Therefore, a PEG of 35,000 Da was used as the feed solute. The PEG used in the preparation of the feed aqueous solution was supplied by Merck-Schuchardt (Germany).

The experiments were performed at different feed flow rates (1–3 m/s), TMPs (0.1–0.5 MPa), temperatures (15–40°C) and feed concentrations (5–15 g/L). Both the permeate and the retentate were recycled back to the feed tank to maintain a constant feed concentration during the experiments that lasted 7 h until a steady state was achieved. The recovery varied to a large extent with the experimental conditions tested: feed flow rates, TMPs, temperatures, membrane and feed concentration. UF tests were performed with the UF pilot plant described elsewhere [4,16–19]. It consisted of two circuits: one for the circulation of the feed solution and the other one for the circulation of the cleaning solution. The volume of the feed tank (75 L) was big enough and the membrane area (35.5 cm^2) was small enough to ensure that the concentration in the feed tank was constant. 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. The maximum feed flow rate that the pilot provided was 500 L/h. However, the experiments were performed at 100, 200 and 300 L/h.

2.3. Membrane cleaning

The Carbosep M2 membrane was cleaned with an aqueous NaOH solution of 0.2% w/w in deionised water. The membrane cleaning procedure for the Tami MSKT membrane was carried out with a 0.25 g/L NaClO aqueous solution at a pH of 11 achieved by NaOH addition. The NaOH and the NaClO were both supplied by Panreac (Spain).

The cleaning cycle for both membranes was performed in a crossflow regimen and consisted of: rinsing with deionised water (35 min), cleaning with the cleaning solution (1.5 h) and finally rinsing with deionised water (35 min). Every cleaning step was performed at a temperature of 40°C, a TMP of approximately 0 bar and a crossflow velocity of 3 m/s.

The cleaning protocol managed to recover initial membrane pure water permeability. Consequently, the same membrane was used in all the experiments.

3. Methods for the estimation of gel layer concentration

The estimation of the gel layer concentration was performed using three methods. The first method corresponded to the gel-polarization model [20] that describes the relationship between the steady-state permeate flux and both the gel layer concentration and the bulk feed concentration. When membrane retention values are high, the linearization of the gel polarization model is expressed in terms of Eq. (1)

$$J_{Pss} = -k \cdot \ln\left(C_g\right) + k \cdot \ln\left(C_0\right) \quad (1)$$

where J_{Pss} is the steady-state permeate flux, k is the mass

transfer coefficient and C_g and C_0 are the gel layer and the bulk feed concentration, respectively. The demonstration of how to arrive at Eq. (1) was previously reported [20,21].

The gel layer concentration can also be estimated as proposed by Song [x] according to Eq. (2)

$$J_{Pss}{}^3 = \frac{2.25 \cdot \gamma \cdot D^2 \cdot C_g}{L} \cdot \left(\frac{1}{C_0}\right) - \frac{2.25 \cdot \gamma \cdot D^2}{L} \quad (2)$$

where γ is the shear rate, D is the diffusivity and L is the membrane length. The demonstration of how to arrive at Eq. (2) can be found in Song [22].

The third model considered in this work for the estimation of the gel layer concentration is suitable for tubular membranes and turbulent flow. This model [23] is given by Eq. (3). This equation is valid when membrane solute retention is very high. Eq. (3) is analogous to Eq. (1), but it relates the concentration polarization modulus C_g/C_0 with membrane UF process parameters.

$$\frac{C_g}{C_0} = \exp\left(\frac{J_{Pss} \cdot D_{\text{int}}{}^{0.11} \cdot \nu^{0.56}}{0.023 \cdot v_{\text{tang}}{}^{0.89} \cdot D^{0.67}}\right) \quad (3)$$

In Eq. (3) v_{tang} is the crossflow velocity, D_{int} is the internal diameter of the membrane and ν is the kinematic viscosity of the permeate.

4. Estimation of model parameters

The diffusivity (D) of PEG at 25°C can be correlated with the molecular weight (MW) of the molecule by means of Eq. (4) [24,25].

$$D = 9.82 \cdot 10^{-9} \cdot (\text{MW})^{-0.52} \quad (4)$$

The density (ρ) and the dynamic viscosity (μ) of the permeate were considered to be equal to those of water at the same temperature [24]. The kinematic viscosity (ν) was calculated from the values of density and dynamic viscosity according to Eq. (5).

$$\nu = \frac{\mu}{\rho} \quad (5)$$

The shear rate is estimated by means of Eq. (6).

$$\gamma = 8\frac{v_{tang}}{D_{\text{int}}} \quad (6)$$

5. Results and discussion

The estimation of the gel layer concentration according to the gel-polarization model [Eq. (1)] [20] and according to the model proposed by Song [Eq. (2)] [22] was performed for the Tami MSKT membrane in Figs. 1 and 2, respectively. The experimental data used in the estimation of the gel layer concentration in Figs. 1 and 2 correspond to the three tested feed concentrations, 5, 10 and 15 g/L, while the operating conditions selected were those that favour gel layer formation the most, i.e. the highest TMPs, 0.4 and 0.5 MPa, and the lowest crossflow velocity, 1 m/s. The gel layer concentration estimated with the gel-polarization model [Eq. (1)] [20] was 37.13 kg/m^3, whereas the gel layer concentration estimated with the model proposed by Song [Eq. (2)] [22] was 19.21 kg/m^3. Bhattacharjee and Bhattacharya [15] reported that a gel layer formed over the membrane surface in the UF of PEG in a stirred cell. They found that gel concentration was a function of the applied pressure and stirring speed (see Fig. 4 in [15]). Other authors also confirmed that the gel layer concentration depended on the crossflow velocity [26]. Membrane permeability and the amount of solute retained by the membrane are directly connected with

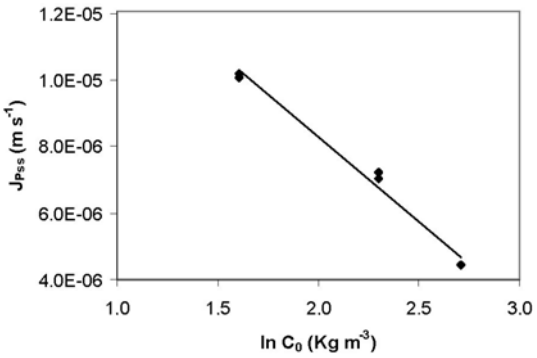

Fig. 1. Estimation of the gel layer concentration from experimental data according to the gel-polarization model [Eq. (1)] for the Tami MSKT membrane.

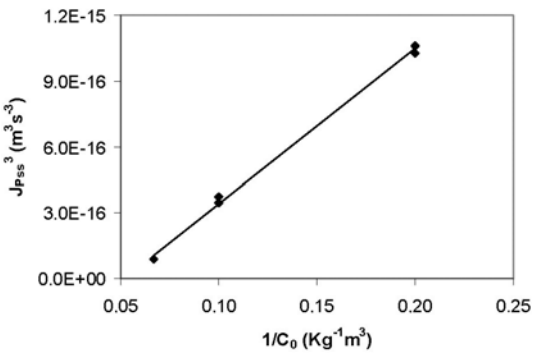

Fig. 2. Estimation of the gel layer concentration from experimental data according to the model proposed by Song [Eq. (2)] for the Tami MSKT membrane.

solute accumulation and compaction over the membrane surface. Therefore, the gel layer concentration is a function of the membrane characteristics. It must be remarked that, as the gel layer concentration depends on operational parameters (TMP, crossflow velocity, etc.), on the properties of the feed solution (feed concentration, solute diffusivity, etc.) and on the hydrodynamic properties of the UF system, it is more accurate to estimate different values of the gel layer concentration for each UF test performed under different experimental conditions. This was considered in the estimation of the gel layer concentration according to the third model contemplated in this work [Eq. (3)]. The results are shown in Table 1. The results must be analyzed carefully because the gel layer may not form for all the experimental conditions tested. The mean value for the gel layer concentration for the Tami MSKT membrane estimated according to Eq. (3) was 17.98 g/L. This value was estimated from the same experimental data used in the estimation of the gel layer concentration in Figs. 1 and 2. The mean value for the gel layer concentration for the Tami MSKT membrane estimated according to Eq. (3) is similar to the one obtained using Eq. (2). However, significant differences were observed in comparison with the result obtained with Eq. (1). This suggests that Eq. (1) may be less suitable for the gel layer concentration estimation than Eqs. (2) and (3).

The values reported in Table 1 for the gel layer concentration that correspond to the Carbosep M2 membrane are higher than those reported for the Tami MSKT membrane for the same experimental conditions. This is consistent with the fact that a higher permeate flux favours the flow of solute molecules towards the membrane surface and a higher accumulation of them in the gel layer formed on the membrane surface. Therefore, there is a higher accumulation of the retained solute over the Carbosep M2 membrane because the permeability of this membrane is higher than the permeability of the Tami MSKT membrane, as this membrane has a higher MWCO.

Table 1
Values of the gel layer concentration estimated according to the third model considered in this work [Eq (3)] for the Tami MSKT and Carbosep M2 membranes

CFv (m/s)	TMP (MPa)	Tami MSKT			Carbosep M2
		C_0 = 5 g/L	C_0 = 10 g/L	C_0 = 15 g/L	C_0 = 5 g/L
1	1	—	—	—	1176
	2	920	1660	2120	1305
	3	1106	1807	2261	1469
	4	1244	1887	2240	1574
	5	1256	1917	2242	—
2	1	—	—	—	983
	2	685	1409	1987	1171
	3	837	1650	2153	1343
	4	931	1783	2234	1393
	5	1005	1835	2321	—
3	1	—	—	—	874
	2	626	1264	1860	1055
	3	743	1434	2042	1232
	4	816	1592	2137	1341
	5	852	1665	2210	—

6. Conclusions

It is more accurate to estimate a different value of the gel layer concentration for each UF test performed under different experimental conditions. However, the results must be analyzed carefully because the gel layer may not form for all the experimental conditions tested.

For the Tami MSKT membrane estimated values of the gel layer concentration for Eqs. (1)–(3) were 37.13, 19.21 and 17.98 kg/m^3. Therefore, the gel-polarization model [Eq. (1)] may be less suitable for gel layer concentration estimation than the model proposed by Song [Eq. (2)] and the third model considered in this work [Eq. (3)]. The estimated value of the gel layer concentration was around 18.6 kg/m^3.

The values reported for the gel layer concentration that correspond to the Carbosep M2 membrane are higher than those reported for the Tami MSKT membrane for the same experimental conditions. Therefore, a higher permeability results in a higher estimated gel layer concentration.

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