Analysis and optimization of the influence of operating conditions in the ultrafiltration of macromolecules using a response surface methodological approach.

Manuel-César Martí-Calatayud[a], María-CintaVincent-Vela*[a], Silvia Álvarez-Blanco [a], Jaime Lora-García[a], Enrique Bergantiños-Rodríguez[b]

[a]*Department of Chemical and Nuclear Engineering, Polytechnic University of Valencia, C/Camino de Vera s/n 46022 Valencia, Spain. Tel. +34 963877000 Ext. 76383; Fax. +34 963877639; e-mail: mamarc13@etsii.upv.es, mavinve@iqn.upv.es, sialvare@iqn.upv.es, jlora@iqn.upv.es*

[b]*Department of Chemical Engineering, Polytechnical Institute José A. Echeverría, Ave. 114, No. 11901, Havana, Cuba. e-mail: enrique_br@quimica.cujae.edu.cu*

*Corresponding author. mavinve@iqn.upv.es

Abstract

In this work, the ultrafiltration of macromolecules was analysed using a response surface methodological approach. The behaviour of two different inorganic membranes was investigated. The membranes selected were a Carbosep M2 membrane (Orelis, France) with a molecular weight cut-off (MWCO) of 15 kDa and a Tami MSKT membrane (Tami Industries, France) with a MWCO of 5 kDa. The solute employed was polyethylene glycol of 35 kDa molecular weight. The influence of transmembrane pressure (0.1, 0.2, 0.3, 0.4 and 0.5 MPa), crossflow velocity (1, 2 and 3 m/s) and feed concentration (5, 10 and 15 g/L) on permeate flux and permeate flux decline was investigated. Analysis of variance was proved to be a useful tool to determine the effect of operating variables on both parameters. The method used demonstrated the presence of coupled effects between factors as well as squared effects that are relevant to the ultrafiltration process. The surface contours obtained from fitted models were used for the optimization of the operating conditions. The goal was to simultaneously maximize the average permeate flux and minimize the flux decline. The optimal operating conditions for the Carbosep M2 membrane were a transmembrane pressure of 0.38 MPa and a crossflow velocity of 3 m/s. The optimal operating conditions for the Tami MSKT membrane could not be determined by means of multiple response optimization due to the low accuracy of the regression model obtained for the cumulative permeate flux decline (SFD) response variable.

Keywords: Ultrafiltration, flux decline, macromolecules, response surface methodology, optimization

1. Introduction

Membrane processes are clean separation techniques with many applications in different areas, such as the dairy industry [1], protein bioseparation [2], waste water treatment [3], the removal of heavy metals [4], etc. Lately, due to a more restrictive legislation concerning urban and industrial wastewaters and the necessity of a more responsible use of water resources, the utilization of membrane separation processes and specially ultrafiltration (UF) is growing fast. Although membrane processes show a great number of applications and advantages, they also have several drawbacks. One of the principal limitations is the decrease of permeate flux with time, which is mainly due to membrane fouling.

Permeate flux decline in UF is mainly caused by two phenomena: the formation of a gel layer on the membrane surface and the obstruction of membrane pores. Moreover, other physical or chemical mechanisms that contribute to membrane fouling can also take place, such as physical adsorption, deposition of molecules on the membrane surface, interactions between different solutes in the feed stream, formation of complexed species, etc.

Membrane fouling causes a reduction of permeate flux, which also causes changes in selectivity and decreases the overall process productivity. Permeate flux can be restored by means of cleaning procedures, but the process must be stopped and great amounts of chemicals, energy, water and time are consumed. Moreover, successive membrane cleaning can reduce membrane lifetime. If the factors that affect flux decline are known, this phenomenon can be better controlled and the best operating conditions can be chosen to increase the permeate flux, thus resulting in a more profitable process.

Many authors have investigated the influence of different factors on flux decline such as S. Hong et al. [5], who analysed the influence of concentration, pressure, particle size and crossflow velocity by means of simple observation of experimental data. In recent years other authors, such as L. Cheng et al. [6] used artificial neural networks to investigate the effect of different variables on flux decline. On the other hand, Response

Surface Methodology (RSM) is a powerful tool that has not been widely used in the determination of the best operating conditions for the minimization of flux decline.

Membrane fouling is a complex phenomenon that is affected not only by the operating conditions, membrane properties and feed characteristics; but also by the complex interactions among all these factors [1]. The effect of one factor on the UF process can be different depending on the values of the other parameters. Therefore, it is of special interest to investigate how all these parameters interact between them in order to perform the optimization of the process. RSM allows the detection of all these interactions, thus making feasible the overall optimization of the process.

The main goal of this paper is to investigate the type of membranes for what the RSM is valid. Moreover, this work determines the influence of different factors on permeate flux decline in UF for these membranes. Data of flux decline from two different membranes and different operating conditions were analysed employing a statistical multifactorial analysis of experimental data. The influence of transmembrane pressure (TMP), crossflow velocity (CFV) and feed concentration (FC) on the average permeate flux and a permeate flux decline indicator was investigated. Statistical multifactorial analysis of experimental data is a useful tool for analysing the influence of different factors and their interactions on a response variable. Moreover, it allows to select the best operating conditions by means of a regression.

2. Experimental

2.1. Materials

For the preparation of the feed solutions PEG of synthesis grade supplied by Merck-Schuchardt (Germany) of 35 kDa molecular weight was used. PEG was selected as the feed solute because it has been very often used as a standard macromolecule in fouling ultrafiltration tests carried out for modelling purposes [7, 8] The preparation of the cleaning solutions was performed using chemically pure NaOH in pellets and a 10% (w/v) NaClO solution, both supplied by Panreac (Spain). All the solutions were prepared with deionised water.

Two different monotubular ceramic membranes were used for the experiments: Carbosep M2 provided by Orelis, S.A. (France) and Céram Inside – MSKTT02510010 membrane from Tami Industries (France). Both membranes have the same dimensions: a length of 0.2 m, an internal diameter of $6 \cdot 10^{-3}$ m, an external diameter of $1 \cdot 10^{-2}$ m and an effective area of $3.55 \cdot 10^{-3}$ m^2. The main characteristics of both membranes are shown in Table 1.

All the experiments were carried out in a typical UF pilot plant consisting in two differentiated circuits: one for the UF experiments and the other one for the cleaning of the membrane. The pilot plant was equipped with a temperature control system and it was described somewhere else [9]. The first set of experiments was performed with the Carbosep M2 membrane. In order to test two membranes with similar characteristics (see Table 1), the Tami MSKT membrane was also selected. Therefore, a second set of experiments was performed with the latter membrane.

2.2. **Crossflow ultrafiltration experiments**

2.2.1. **Fouling experiments**

The experiments were performed at a constant temperature of 25ºC. Permeate flux was gravimetrically measured at different time intervals. The experiments with the Carbosep M2 membrane were performed at different TMPs (0.1, 0.2, 0.3 and 0.4 MPa) and CFVs (1, 2 and 3 m/s), maintaining FC constant at 5 g/L. However, in the experiments carried out with the Tami MSKT membrane, FC was varied too. Table 2 summarizes the operating conditions tested. Differences in selected TMP ranges for both membranes were due to the very low permeate flux obtained with the Tami MSKT membranes with the lowest TMP tested. It was not possible to measure this low permeate flux with the required precision during the experiments.

Each run was stopped after 7 hours of operation, when a quasi-stationary permeate flux was reached. After each experiment, the membranes were cleaned and their permeability was checked with deionised water at 25ºC, a TMP of 0.3 MPa and a CFV of 3 m/s.

2.2.2. **Cleaning procedure**

After each run the Carbosep M2 membrane was cleaned following the stages that are reported below at a constant temperature of 50ºC, a TMP slightly lower than 0.1 MPa and a CFV of 3 m/s:

1. Rinsing with deionised water during 35 min.
2. Cleaning with a NaOH solution of 0.2% (w/w) during 1.5 hours.
3. Rinsing with deionised water during 35 min.

The Tami MSKT membrane was cleaned with the same procedure, but in the second stage a 250 ppm NaClO solution was used. Additionally, NaOH was added up to a pH value of 11. After the cleaning step, the water permeability was checked as described previously. The initial water permeability of the membranes was completely recovered after each cleaning cycle.

3. Methodology

3.1. Response Surface Methodology

Response Surface Methodology (RSM) is a statistical method of data analysis that allows a better understanding of a process than the conventional methods of experimentation, because it is able to predict how the inputs affect the outputs in a complex process where different factors can interact among them [4, 10-12]. It is a useful tool to identify and quantify the effects of the factors that participate in a process. The main objective of RSM is the determination of the optimal operating conditions or the identification of the causes involved in any operating problem. In order to obtain a reliable analysis, a statistical multifactorial analysis of experimental data must be properly done. In the statistical multifactorial analysis of experimental data all factors are varied simultaneously.

When more than one factor is varied, it is possible to identify not only the first order influence of the factors, but also higher order influences of the factors on the variable of study. Moreover, the effect of one factor could be different depending on the value of other factors. When this happens, there is an interaction between both factors due to a coupled effect. The RSM is able to predict the interaction effects among the considered factors. In this paper, the influences of TMP, CFV and FC on the variation of permeate flux with time were analysed by means of a statistical multifactorial analysis of experimental data. The different conditions tested for each factor are shown in Table 2.

Experimental data can be employed to evaluate the regression coefficients of a polynomial equation that correlates a dependent variable with several independent variables. These regression coefficients can give information not only about the influence of the individual factors, but also about the effects among them. In the conventional methods of experimentation the influence of one factor is evaluated, while the rest of the factors are maintained constant. However, in RSM all factors are varied simultaneously, thus all the complex conjugated effects are taken into account. The response model can be used for the optimization of the process [4, 10, 13]. To analyse what operating conditions, squared effects and interactions among factors are more significant in the response variable, all the coefficients of the different polynomial equations were tested for significance with an analysis of variance (ANOVA), which is explained in the following section.

3.2. **Statistical analysis**

ANOVA is a powerful statistical technique that studies the effects of a set of factors on the mean of one variable. ANOVA decomposes the total variability of the response variable in the effects of each factor of study and their possible interactions plus a residual part related to the uncontrolled factors and variability occurred by chance. By means of this technique, the error variance can be estimated as well as the relative contribution of each factor. The ANOVA technique is thoroughly described in the literature [11, 12].

The ANOVA procedure calculates the degrees of freedom, the sum of squares, the mean square, the F-ratio and the p-value. Degrees of freedom are related with the number of levels analysed for each factor and they are employed in the calculation of the mean squares. For each factor or coupled interaction studied, the ANOVA table employs one degree of freedom and the rest of them are used for estimating the variability which is caused by random. The sum of squares is the sum of the squares of deviations from the mean, and the mean square is equal to the sum of squares divided by the degrees of freedom. It is possible to associate a part of the total variability with each factor of study by calculating the mean squares corresponding to all the factors and interactions studied.

The mean square is an estimator of the variance of the data. Residuals are the part of an observation caused by the variability of the factors that are not controlled in the experiment, that is to say the random variability. The ratio between the mean square of a factor and the mean square of residuals predicts if such factor has a noticeable influence on the variable of study. This ratio between both mean squares is known as F-ratio. The F-ratios are compared to tabulated F-ratios obtained from Fisher distribution tables. Then the parameter known as p-value measures the probability that the tabulated F-ratio is higher than the experimental F-ratio. This parameter represents the probability that the variation associated to a factor may have occurred by chance. Therefore, the lower the p-value is, the more significant the influence of a factor on the response variable is. As a rule, it is assumed that a p-value lower than 0.05 means that the current factor has significant influence on the results [11, 12]. Furthermore the standardized effect of each factor on the response variable can be calculated in order to compare which one has a greater influence. There is also a level of significance for the ANOVA that distinguishes between the influent variables and the non influent ones.

3.3. **Response variables of study**

C. Cojocaru et al. studied in a previous paper [4] the effect of different operating conditions on UF experiments in order to optimize the copper removal by means of maximizing the average permeate flux and minimizing the permeate flux decline employing the RSM. In such work the utility of statistical multifactorial analysis of experimental data for understanding the effects of different factors and their interactions on a process was proved.

In the present work, the influence of different operating conditions on permeate flux was analysed by means of RSM. In order to evaluate the volume of permeate obtained per unit of time and membrane area, the response variable chosen was the average permeate flux, which was calculated by means of the following equation:

$$\overline{J_P} = \frac{1}{t_N} \cdot \int_0^t J_P(t) \cdot dt \qquad (1)$$

Where $J_P(t)$ is the permeate flux evolution along the time obtained from experimental data, t is the time of operation and t_N is the time corresponding to the last value of permeate flux considered. The permeate flux evolution with time was interpolated from the experimental data of permeate flux obtained at different time intervals as it is explained in section 4.1.

Moreover, the other purpose of the statistical study was to analyse the effect of the operating conditions on flux decline. The response variable chosen for this purpose was the cumulative flux decline (SFD) which is defined by the following equation [4]:

$$SFD = \sum_{i=1}^{N} \frac{J_P(0) - J_P(i)}{J_P(0)} \qquad (2)$$

where N is the point corresponding to the end of the experiment, when the quasi stationary flux is achieved; $J_P(0)$ is the initial permeate flux and $J_P(i)$ is the permeate flux at different operating times. This parameter summarizes the information on the evolution of permeate flux with time throughout the experiment (and not only for one specific time). Therefore, by means of this parameter flux decline can be characterized. Then the greater the SFD is, the faster and more noticeable the flux decline is, thus indicating that membrane fouling is more severe.

4. Results and discussion

4.1. Data treatment

The experimental data of permeate flux were plotted versus time (Figs. 1-4). As some experimental error may occur, the data were smoothed using the Mathcad® supsmooth tool. Afterwards, the smoothed data were interpolated and a regression model was obtained. Mathcad supsmooth tool uses linear least square fitting for this purpose [14].

4.2. Experimental results

The curves that represent the evolution of permeate flux with time usually show a shape composed by two regions: the first one where the permeate flux declines very sharply, and a second region where the permeate flux declines more slowly until a quasy stationary permeate flux is reached. Fig. 1 shows an example of the experimental results obtained for the Carbosep M2 membrane at different TMPs. A fast reduction of permeate flux can be observed at the beginning of the process. This reduction is more severe at high TMPs.

An example of the experimental results obtained for the Tami MSKT membrane at the same operating conditions is shown in Fig. 2. It can be observed that flux decline is more severe for the Carbosep M2 membrane, but the values of permeate flux are higher for this membrane as it has a larger pore size. Higher TMPs result in higher permeate fluxes. In order to quantify the effect of the operating conditions on average permeate flux and cumulative flux decline, a statistical analysis was performed and commented in the next sections.

Figs. 3 and 4 show the experimental results obtained for both membranes at a CFV of 2 m/s and a feed concentration of 5g/L. It occurs the same as in Figs. 1 and 2, a higher permeate flux decline was observed for the Carbosep M2 membrane. It can also be observed that permeate flux increases with CFV as expected.

4.3. **Effect of operating conditions on average permeate flux**

4.3.1. **Carbosep M2 membrane**

Two independent variables were chosen to perform the statistical analysis: TMP (A) and CFV (B), whereas the average permeate flux was chosen as the response variable. The fitting equation obtained for the Carbosep M2 membrane was the following:

$$\overline{J_P} = 0.507 + 107.084 \cdot A + 20.726 \cdot B - 90.183 \cdot A^2 + 30.914 \cdot A \cdot B - 1.964 \cdot B^2 \qquad (3)$$

0.1 < A < 0.4 MPa   1 < B <3 m/s

Table 3 shows the ANOVA table obtained for the average permeate flux for this membrane. ANOVA table includes the sum of squares, degrees of freedom, mean square, F-ratio, p-value and standardized effect for each factor studied and their interactions.

As it was explained in section 3.2., if the p-value of one factor is lower than 0.05, this factor has a significant influence on the response variable. In adittion, the magnitude of each effect can be determined by means of the standardized effect. For each ANOVA study there is a level of significance, that is surpassed only by the standardized effect of one factor if its p-value is lower than 0.05. Then, the more the standardized effect of one factor surpasses the level of significance, the higher the influence of this factor on the response variable is.

The statistical analysis results for average permeate flux for the Carbosep M2 membrane illustrate that both the TMP and CFV have a remarkable influence on average flux, since they have a p-value practically equal to zero. However, the squared effects are not significant enough, while the interaction between CFV and TMP is in the limit of significance with a p-value close to 0.05. It has to be noted that the level of significance was estimated at 2.45, therefeore the factor whose standardized effect is much higher than this value has the greatest influence on the response variable. Hence, the factor with the greatest influence on average flux is CFV followed by TMP. The standardized effects of both factors are positive, which means that average flux increases as CFV and TMP are raised. The influence of the interaction between both factors is positive too, but it is not significant enough because its standardized effect is lower than 2.45. Fig. 5 shows the average flux calculated for all the range of values of CFV at the maximum and minimum levels of TMP tested. By means of this figure it is possible to analyse the influence of the interaction between both operating conditions. As TMP raises, the average flux increases, but this increase is higher at higher values of CFV, which confirms the positive interaction. Nevertheless, the standardized effect of the interaction is below the level of significance, so it is not considered statistically significant.

Fig. 6 represents the surface contours for the estimated response variable as a function of the factors studied. The maximum average flux was obtained at the maximum values of CFV and TMP tested. Nevertheless, higher values of those parameters represent greater costs and could result in higher flux decline.

4.3.2. **Tami MSKT membrane**

As it is shown in Table 2, for this membrane the influence of three variables (TMP (A), CFV (B) and FC (C)) on average flux was evaluated. When a statistical analysis is performed with three factors of study, interaction effects among factors can be determined. Nevertheless, for scientific interpretation, main effects and interaction effects are more descriptive. The regression equation obtained from the experimental data considering interaction effects among factors for this membrane is the following:

$$\overline{J_P} = -12.725 + 157.497 \cdot A + 6.590 \cdot B + 1.167 \cdot C - 158.253 \cdot A^2 + 34.423 \cdot A \cdot B - 5.432 \cdot A \cdot C - \\ - 3.323 \cdot B^2 + 0.303 \cdot B \cdot C - 0.065 \cdot C^2 \qquad (4)$$

0.2 < A < 0.5 MPa   1 < B <3 m/s   5 < C <15 g/L

Table 4 shows the results of the ANOVA for average permeate flux for the Tami MSKT membrane. These results confirm that all possible factors and interaction effects are influential on average permeate flux because all of them have p-values lower than 0.05. CFV and TMP show the greatest influence on average permeate flux because their standardized effects are the highest. These variables have a positive effect on average permeate flux. FC has a negative influence, but the effects of TMP and CFV are greater. Moreover two interaction effects have also greater influence on average flux than TMP. These two interaction effects are related to TMP, so to achieve the best operating conditions it is preferred taking into account the coupled effects of TMP with other factors than the direct influence of TMP. The influence of FC on average flux resulted to be negative and the second in order of importance. Then, the less concentrated the feed is, the greater the average permeate flux is.

The influence of coupled effects is more significant for this membrane than for the Carbosep M2 membrane. In Figs. 7-9 the values of average permeate flux are plotted as a function of different variables in order to analyse the influence of the interactions. The effect of the interactions between TMP and the other two factors can be observed to be remarkable. While the interaction between TMP and CFV is positive, the interaction between TMP and FC is negative because the highest values of average permeate flux are obtained for the lowest FC. In Fig. 7 it can be observed that at low values of TMP (0.2 MPa) the difference between the average permeate flux obtained at 1 and 3 m/s is not very high, but at high values of TMP the significance of CFV becomes greater. Something similar can be observed for the interaction between TMP and FC plotted in Fig. 8: at higher values of TMP the difference in average permeate flux between the experiments at low and high FC is greater. With regards to the interaction between CFV and FC, its influence is smaller since the standardized effect is lower than the level of significance. The lower significance of this interaction can be observed in Fig. 9, because at high values of CFV (3 m/s) the difference between the average flux at high and low levels of FC is smaller but similar to that observed at low values of CFV (1 m/s).

Other important influences are those due to squared effects of factors like TMP and CFV. As it can be observed in Table 4, these interactions effects have a negative effect on average permeate flux while their main effects are positive. Therefore the understanding of the real influence of these factors on average flux is more difficult. This squared effect is more pronounced in the case of TMP, while the significance of the linear and the squared effect is very similar. This result agrees with the assumption that there is a limit in the positive influence of TMP and CFV on average permeate flux due to membrane fouling and cake build-up. Then, there is a need for analysing the influence of these factors on flux decline, which is reported in section 4.4.

Due to the main effects, interaction effects and squared effects, the global effect of each factor is better understood from the response surface plots shown in Figs. 10 and 11. The data shown in these figures are in agreement with the conclusions obtained attending to the main effects: to achieve high average permeate flux, the best operating conditions are high values of TMP and CFV and low values of FC. These results confirm the expected effect of each factor but they are submitted to different interactions among those factors.

TMP is the driven force of the UF process, which explains its positive effect on permeate flux. Nevertheless the effect of TMP is restricted because there is a squared effect that has negative influence on average permeate flux, which is related to pore blockage and the formation of the gel layer. Regarding to gel layer formation, as TMP increases, the particles are more compressed, their ability to return to the bulk solution is reduced and the thickness of the gel layer increases [15, 16]. This phenomenon could explain the shape of the curves of permeate flux versus TMP shown in Figs. 2 and 3 where the values of the stationary permeate flux become independent of TMP at high values of TMP, and then the process becomes mass transfer-controlled [1, 15-17]. The formation of a gel layer could cause that, above a certain TMP the average permeate flux decreases with an increase in TMP. This behaviour can be explained by means of the regression model predicted by ANOVA, due to the negative influence of the squared effect of TMP on average flux. The experimental results confirm that the effect of the gel layer is more intense in the case of the Tami MSKT membrane because the squared effects are significant. This is due to the fact that the MWCO of the Tami MSKT membrane is lower; therefore a larger amount of molecules can accumulate on the membrane surface. That difference between both membranes can also be observed from Figs. 6 and 10: in the case of the Carbosep M2 membrane, the iso-average permeate flux contours are close to a straight line while for the Tami MSKT membrane they are more curved due to the influence of the squared effect and the interactions among the variables.

On the other hand, as CFV increases higher values of average permeate flux are obtained. Many authors have reported that at the first stages of crossflow filtration there is no influence of CFV on permeate flux [2, 5], while the effect of CFV is attributed to the "self-cleaning" of the membrane in the later stages of the UF process. This variable is related to membrane fouling and it has a great influence on the SFD, what will be analysed in section 4.4. As CFV increases, more turbulence is created near the membrane surface and therefore a larger amount of particles are removed from the membrane surface. Therefore, fouling is expected to decrease with CFV as the thickness of the gel layer is reduced. This factor has also a significant squared effect on average permeate flux for the Tami MSKT membrane. This squared effect has a negative influence on average permeate flux and it can be related to the limit in the "self-cleaning" of the membrane. At high velocities, the greatest particles of solute can be removed away from the membrane surface, allowing the insertion of smaller molecules close to the surface and promoting the stratification of the particles on the membrane surface according to their size, thus causing the compression of the fouling layer, increasing its hydraulic resistance and allowing a higher pore plugging. The effect of

CFV on average permeate flux is also related to the interaction between TMP and CFV, since the counterproductive effect of CFV occurs at high TMPs when the lateral forces caused by CFV are lower than the driven force due to TMP that transports the particles towards the membrane surface. The effect of CFV on average permeate flux and the interaction of CFV with TMP that have been observed in this work are in agreement with the findings and explanations reported by Cheryan et al. [1]. ANOVA table reveals that the squared effect of CFV for the Carbosep M2 membrane is less significant. Therefore, for this membrane the increase of CFV is also effective at high TMPs due to its higher MWCO. This implies a lower retention of solute molecules on the membrane surface and that the stratification of molecules becomes more difficult. It has to be also noted that the experiments with the Carbosep M2 membrane were only carried out at a FC of 5 g/L, while for the Tami MSKT membrane greater FC were considered as well (5, 10 and 15 g/L). At higher FC the squared effect of CFV could be more significant.

Regarding the effect of FC on average permeate flux, as it was commented this influence is negative, as expected. As FC increases membrane fouling is more severe as reported by several authors [1, 15]. Regarding the squared effects and interactions of FC, almost all of them lead to a decrease in average permeate flux. Higher FC causes a greater accumulation of particles on the membrane surface, and then the minimum concentration of solutes required to form a gel layer is easily reached. However, Table 4 shows a positive coupled effect of FC and CFV on average permeate flux. This can be explained considering that the positive influence of CFV is higher than the negative influence of FC, resulting in a global positive influence of the combination of these two factors. In fact, as the standardized effect of CFV is slightly higher than that of FC, the positive coupled effect is low. The coupled effect of FC and CFV on average permeate flux can also be observed in Fig. 9. As CFV increases the influence of FC on average permeate flux is slightly lower, as expected. This is due to the fact that high CFVs prevent the deposition of feed solutes over the membrane surface.

4.4. **Effect of operating conditions on permeate flux decline**

4.4.1. **Carbosep M2 membrane**

The regression model that relates permeate flux decline with TMP (A) and CFV (B) resulted to be the following:

$$SFD = -9.549 + 546.998 \cdot A - 33.352 \cdot B + 1015.570 \cdot A^2 - 333.929 \cdot A \cdot B + 21.130 \cdot B^2 \quad (5)$$

$0.1 < A < 0.4$ MPa $\quad 1 < B < 3$ m/s

Table 5 shows the ANOVA table obtained. It can be observed that both factors (TMP and CFV) as well as their coupled effect have significant influence on SFD because their p-values are lower than 0.05 and their standardized effects are higher than the level of significance. The squared effects of TMP and CFV have a p-value higher than 0.05, so they do not have remarkable influence on the response variable. It can also be observed from the sign of the standardized effect that permeate flux decline increases with TMP, while it decreases with CFV. It has to be pointed out that the interaction between TMP and CFV has a noticeable influence on SFD. In Fig. 12, SFD is plotted as a function of TMP and CFV. From that figure, the effect of the interaction between both variables on SFD can be observed. At low values of TMP, the effect of an increase in CFV is lower than in the case of high TMP, as it was expected, and the variations could be due to the experimental error committed [18]. On the other hand, at high values of TMP the same increase in CFV entails an improvement of the UF process because permeate flux decline is significantly reduced, thus the values of SFD becoming very similar for the highest and lowest values of TMP. Moreover, the standardized effect for this interaction is much higher than the level of significance. The reason for the great interaction between both variables can be the higher amount of molecules that are transported towards the membrane surface as TMP rises. Therefore, the effect of CFV on permeate flux decline is more pronounced at the higher TMPs. It has to be noted that the regression coefficient of the model predicted by ANOVA is lower than that obtained for the average permeate flux analysis. Nevertheless, the model fits well the experimental data in most of the conditions tested.

The optimal conditions that cause the lowest permeate flux decline can be observed in Fig. 13. TMP has a greater influence on permeate flux decline than CFV. Although a high TMP is required to obtain a high average permeate flux, TMP should be low in order to reduce permeate flux decline. Therefore, an intermediate solution should be found to treat high volumes of liquid streams with low values of fouling in order to improve the performance of the process. A possible approximation to this intermediate solution is discussed in section 4.5.

4.4.2. **Tami MSKT membrane**

The regression model obtained for this membrane is the following:

$$SFD = 47.175 - 78.076 \cdot A + 4.880 \cdot B - 4.234 \cdot C + 221.222 \cdot A^2 - 14.420 \cdot A \cdot B - 5.564 \cdot A \cdot C + 1.246 \cdot B^2 - 0.127 \cdot B \cdot C + 0.291 \cdot C^2 \quad (6)$$

$0.2 < A < 0.5$ MPa $\quad 1 < B < 3$ m/s $\quad 5 < C < 15$ g/L

An ANOVA was also performed for SFD for this membrane. Table 6 shows the results of the ANOVA. Squared effects of TMP and FC are significant for SFD response, as their p-values are lower than 0.05. This differs from the results obtained with the Carbosep M2 membrane, where only factors and the coupled effect were significant. The difference could be due to the diferent operating conditions tested for both membranes. Moreover, the analysis for the Tami MSKT membrane resulted to be less accurate, as the regression coefficient is very low. The value of the regression coefficient indicates that only the 56.11% of variability in SFD is explained by the analysis. In addition, when Figs. 1 and 2 are compared, it can be observed that flux decline was more noticeable for the Carbosep M2 membrane. Therefore, the utilization of SFD to characterize permeate flux decline is more quantifiable and representative for such membrane. The adjusted coefficient of determination (R^2_{adj}) is useful to compare models with different number of independent variables. When the R^2_{adj} are compared, it is confirmed that the model fits best to the experimental data for the Carbosep M2 membrane.

The most significant influence on SFD for Tami MSKT membrane is due to the squared effect of FC. Permeate flux decline increases with the amount of particles deposited on the membrane surface, thus increasing the thickness of the gel layer, as it was explained in section 4.3.2. Another significant effect is the interaction between FC and TMP. Their negative coupled effect on SFD may be due to the low accuracy of the regression model obtained for SFD for the Tami MSKT membrane. The remarkable effect of TMP on permeate flux decline can also be noted taking into account the squared effect of TMP, whose standardized effect is higher than the level of significance. The higher the TMP is, the more intense the permeate flux decline is. As the TMP raises, the gel layer thickness and/or its compaction increases, thus increasing the hydraulic resistance to permeation and neutralizing the effect of an increasing driving force [15, 19].

The interaction plot that shows the effect of the interaction among variables on SFD is not presented, since no significant conclusions could be obtained, due to the low accuracy of the model obtained for this membrane. The same occurs with the surface contour plots of SFD. The different behaviour for both membranes can be due to the different active layer and support materials and to the different MWCO, which can affect the fouling mechanism. Figs. 1 and 3 show that Carbosep M2 membranes present a noticeable permeate flux decline in the first moments of operation, which has been attributed by many authors to solute-membrane interactions that result in a quick physical adsorption of the solute on the surface or inside the membrane pores. Related to this, Cheryan [1] reported that solute adsorption on the carbon support of Carbosep membranes is remarkable while it does not occur in the case of membranes with an alumina support, such as Tami MSKT membranes. The MWCO also plays a significant role in the developement of permeate flux decline. As it is shown in Table 1, the MWCO of the Carbosep M2 membrane (15 kDa) is more similar to the molecular weight of PEG molecules (35 kDa) than that of the Tami MSKT membrane (5 kDa). This difference can also affect permeate flux decline because if the size of the molecules is much higher than the pore size it is more difficult that solute molecules can penetrate the membrane and cause internal pore blocking. Then, the more similar in shape and size the particles and the pores are, the greater the permeate flux decline is, as reported by Song [15]. On the other hand, the formation of a gel layer is more feasible in the case of Tami MSKT membrane due to the higher solute rejection, which results in higher concentrations of solute near the membrane surface. Therefore both membranes may be affected by different fouling mechanisms according to the experimental results obtained in this work and to the results reported by other authors [1, 15].

4.5. **Multiple response optimization**

4.5.1. **Carbosep M2 membrane**

There are different methods to perform multiple response optimization. When a fitted model is obtained by means of RSM, the optimization of the operating conditions can be carried out for two response variables simultaneously. For this purpose the contour plots of both response variables can be superimposed. In this case, the goal of the multiple response optimization was to maximize the average permeate flux and minimize the SFD. The optimal operating conditions that were obtained for the Carbosep M2 membrane are shown in Tables 7 and 8.

By means of the optimization performed, an optimal average permeate flux value very close to the maximum experimentally obtained was achieved. However, the optimal value of the permeate flux decline was not close to the minimum experimental value, as it was expected. In this case, as it is shown in Fig. 14, the result of the multiple response optimization is very similar to the one that would be obtained if the goal was only the maximization of the average permeate flux. The optimal value of CFV (represented in

Fig. 14 by a diamond-shape symbol) corresponds to the highest experimental value, while the optimal value of TMP is close to it. As both response variables are related, good values of average permeate flux and SFD could be obtained at the same time. Finally, the multiple response optimization for the Tami MSKT membrane could not be performed due to the low accuracy of the model for the SFD response variable (see Table 6).

5. Conclusions

RSM was demonstrated to be a useful tool to investigate the influence of operating conditions on UF processes and to perform the optimization of the operating conditions simultaneuosly. For those purposes, statistically fitted models were used. High values of TMP and CFV were observed to induce high average permeate fluxes while low FC caused an increase in the average permeate flux. These effects agree with the conclusions of many authors but there is a limitation in such affirmations due to the developement of the gel layer and the fouling of the membranes. By means of ANOVA it is possible to determine opposed effects, which are related to the presence of squared effects and coupled interactions between factors. The results confirm the presence of a critical value of TMP that separates the pressure-controlled UF process from the mass transfer-controlled UF process. When TMP is higher than this value permeate flux does not increase with the applied TMP. The interaction between TMP and CFV shows that this critical TMP increases as CFV raises, due to the contribution of CFV to the "self-cleaning" of the membrane. There is also a limit in the values of CFV, which is related to the stratification of molecules by size in the gel layer.

RSM was also used to investigate the effect of operating variables on permeate flux decline. The lowest flux decline is achieved at medium-high CFVs and low TMPs. The use of RSM was observed to be more adequate when permeate flux decline was noticeable. In the case of the Tami MSKT membrane, a low permeate flux decline was observed, thus explaining the worst fit of the model to the experimental results. Finally, the models obtained by ANOVA were used to optimize the operating conditions to simultaneously maximize the average permeate flux and minimize the permeate flux decline. The optimum conditions were a TMP of 0.38 MPa and a CFV of 3 m/s. The fitted models can also serve as a tool to perform the control of the UF process.

List of symbols

A	- Transmembrane pressure in the fitted models
ANOVA	- Analysis of variance
Av. flux	- Average flux
B	- Crossflow velocity in the fitted models
C	- Feed concentration in the fitted models
CFV	- Crossflow velocity
FC	- Feed concentration
$\overline{J_P}$	- Average permeate flux
$J_P(t)$	- Permeate flux as a function of time
MWCO	- Molecular weight cut-off
PEG	- Polyethylene glycol
R^2	- Coefficient of multiple determination
R^2_{adj}	- Adjusted statistic coefficient

RSM	- Response surface methodology
s^2	- Variance
SFD	- Cumulative permeate flux decline
t	- Time
t_N	- Last time considered
TMP	- Transmembrane pressure
UF	- Ultrafiltration

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Table 1. Membrane characteristics.

Membrane	Active layer	Porous support	MWCO (kDa)	Effective area (m^2)
Carbosep M2	ZrO_2-TiO_2	Carbon	15	35.5
Tami MSKT	Al_2O_3-TiO_2	Alumina	5	35.5

Table 2. Operating conditions tested in the experiments for each membrane.

Membrane	TMP (MPa)	CFV (m/s)	FC (g/L)	Number of experiments
Carbosep M2	0.1, 0.2, 0.3, 0.4	1, 2, 3	5	12
Tami MSKT	0.2, 0.3, 0.4, 0.5	1, 2, 3	5, 10, 15	36

Table 3. ANOVA table for average permeate flux for the Carbosep M2 membrane. (R^2 = 97.87%; R^2_{adj} = 96.10%) Level of significance: 2.45

Source	Sum of squares	Degrees of freedom	Mean square	F-Ratio	p-value	Standardized effect
A:TMP	2300	1	2300	109	0.00	10.4
B: CFV	3394	1	3394	161	0.00	12.7
AA	10	1	10	0	0.52	-0.7
AB	96	1	96	4	0.08	2.1
BB	10	1	10	0	0.51	-0.7
Total error	126	6	21			
Total (corr.)	5936	11				

Table 4. ANOVA table for average permeate flux for the Tami MSKT membrane. (R^2 = 98.83%; R^2_{adj} = 98.43%) Level of significance: 2.04

Source	Sum of squares	Degrees of freedom	Mean square	F-Ratio	p-value	Standardized effect
A: TMP	1688	1	1688	687	0.00	26.2
B:CFV	1684	1	1684	685	0.00	26.1
C:FC	1231	1	1231	501	0.00	-22.4
AA	90	1	90	37	0.00	-6.1
AB	355	1	355	145	0.00	12.0
AC	221	1	221	90	0.00	-9.5
BB	88	1	88	36	0.00	-6.0
BC	37	1	37	15	0.00	3.9
CC	21	1	21	9	0.01	-2.9
Total error	64	26	2			
Total (corr.)	5481	35				

Table 5. ANOVA table for SFD for the Carbosep M2 membrane. (R^2 = 95.17%; R^2_{adj} = 91.14%) Level of significance: 2.44

Source	Sum of squares	Degrees of freedom	Mean square	F-Ratio	p-value	Standardized effect
A:TMP	22457	1	22457	60	0.00	7.7
B:CFV	8356	1	8356	22	0.00	-4.7
AA	1238	1	1238	3	0.12	1.8
AB	11151	1	11151	30	0.00	-5.4
BB	1190	1	1190	3	0.12	1.8
Total error	2255	6	376			
Total (corr.)	46647	11				

Table 6. ANOVA table for SFD for the Tami MSKT membrane. (R^2 = 58.90%; R^2_{adj} = 44.68%) Level of significance: 2.06

Source	Sum of squares	Degrees of freedom	Mean square	F-Ratio	p-value	Standardized effect
A:TMP	27	1	26.71	1	0.42	-0.8
B:CFV	302	1	302	8	0.01	2.8
C:FC	229	1	229	6	0.02	-2.4
AA	176	1	176	4	0.04	2.1
AB	62	1	62	2	0.22	-1.2
AC	232	1	232	6	0.02	-2.4
BB	12	1	12	0	0.58	0.6
BC	6	1	6	0	0.69	-0.4
CC	423	1	423	11	0.00	3.3
Total error	1026	26	39			
Total (corr.)	2496	35				

Table 7. Boundary and optimal values of the operating conditions for the Carbosep M2 membrane.

Factor	Low level	High level	Optimum value
TMP	0.10	0.40	0.38
CFV	1.00	3.00	3.00

Table 8. Boundary and optimal values of the response variables for the Carbosep M2 membrane.

Response	Minimum experimental value	Maximum experimental value	Optimal value
Average permeate flux	34.58	109.29	108.32
SFD	8.29	239.50	55.36

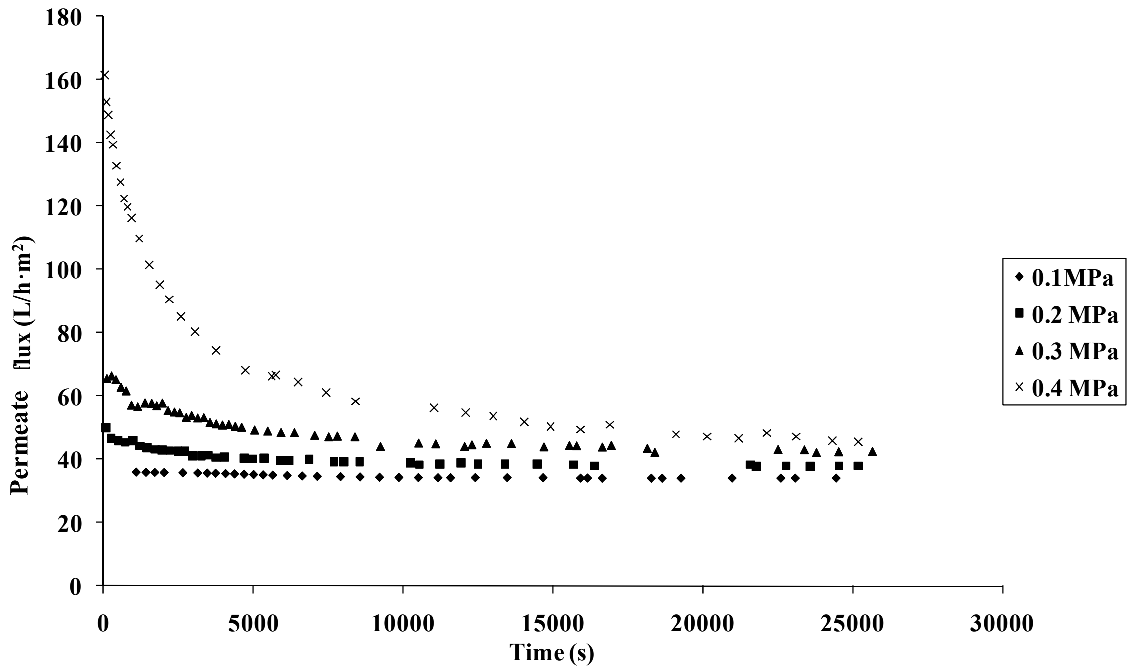

Fig. 1. Experimental data for permeate flux for the Carbosep M2 membrane at different TMPs, at a crossflow velocity of 1 m/s and a feed concentration of 5 g/L.

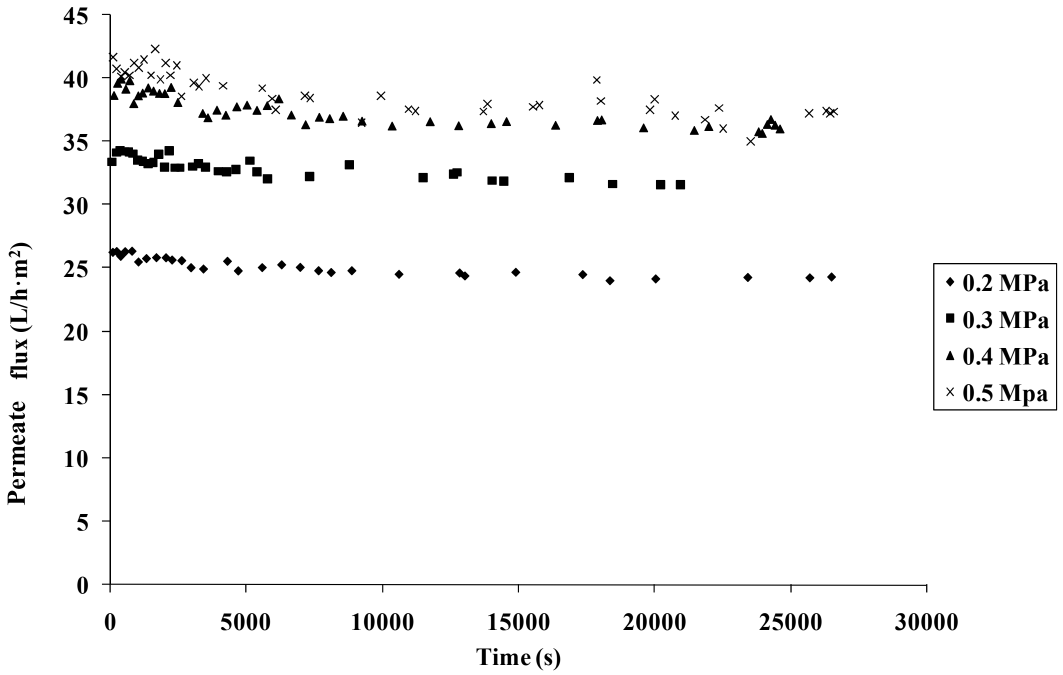

Fig. 2. Experimental data for permeate flux for the Tami MSKT membrane at different TMPs, at a crossflow velocity of 1 m/s and a feed concentration of 5 g/L.

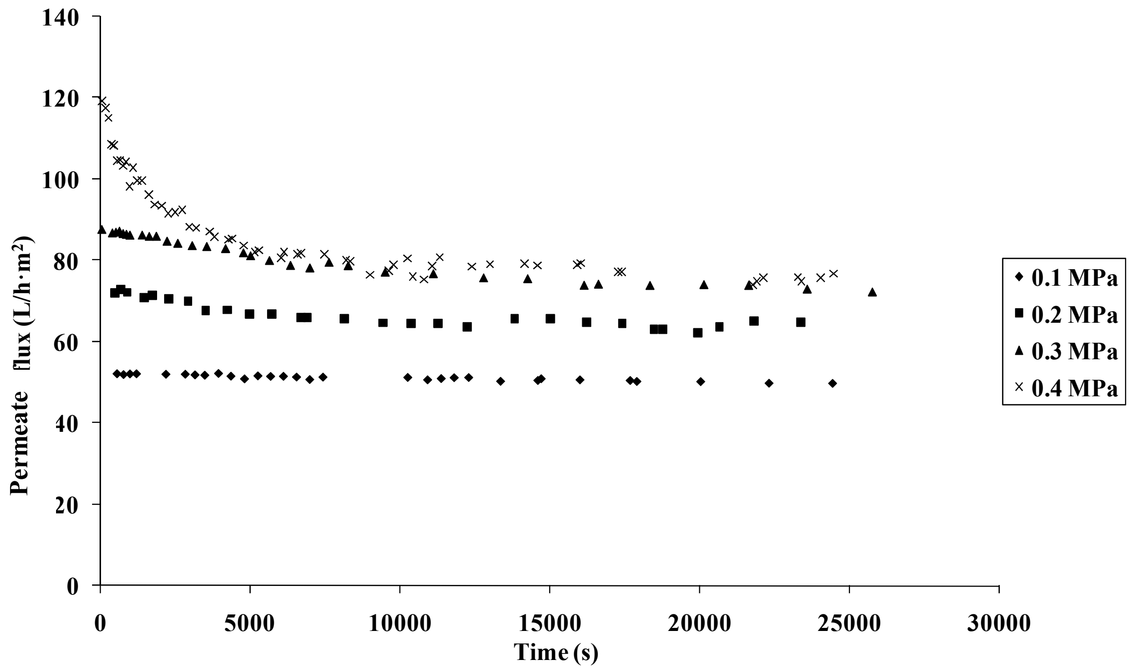

Fig. 3. Experimental data for permeate flux for the Carbosep M2 membrane at different TMPs, at a crossflow velocity of 2 m/s and a feed concentration of 5 g/L.

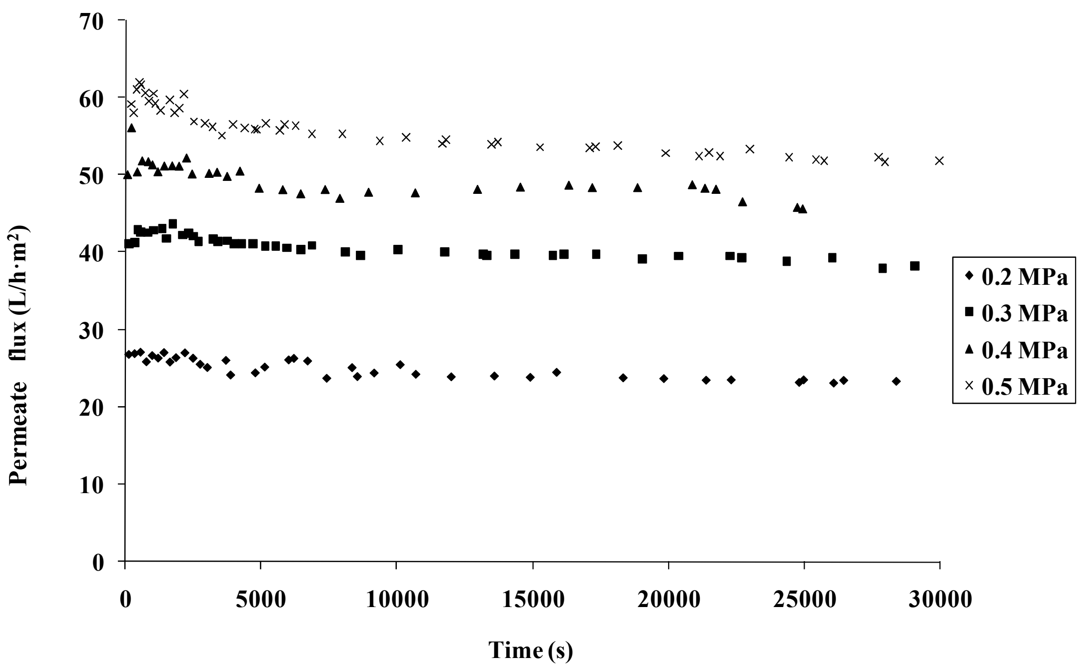

Fig. 4. Experimental data for permeate flux for the Tami MSKT membrane at different TMPs, at a crossflow velocity of 2 m/s and a feed concentration of 5 g/L.

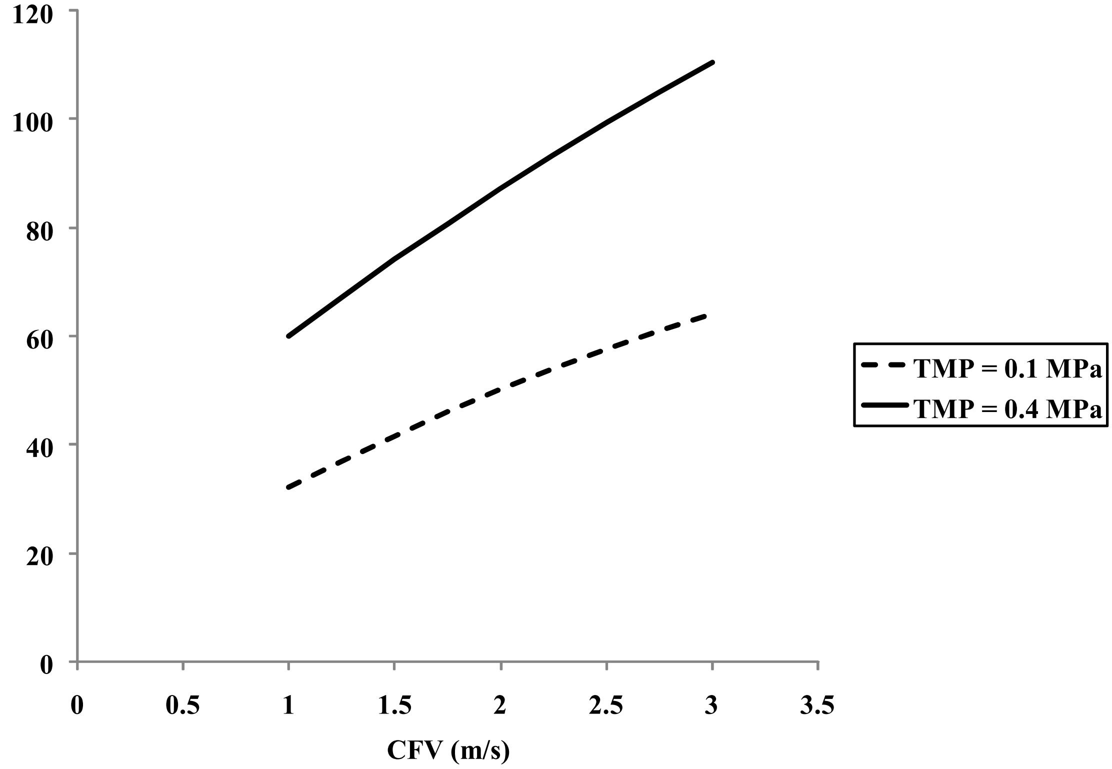

Fig. 5. Interaction plot for average permeate flux for the Carbosep M2 membrane.

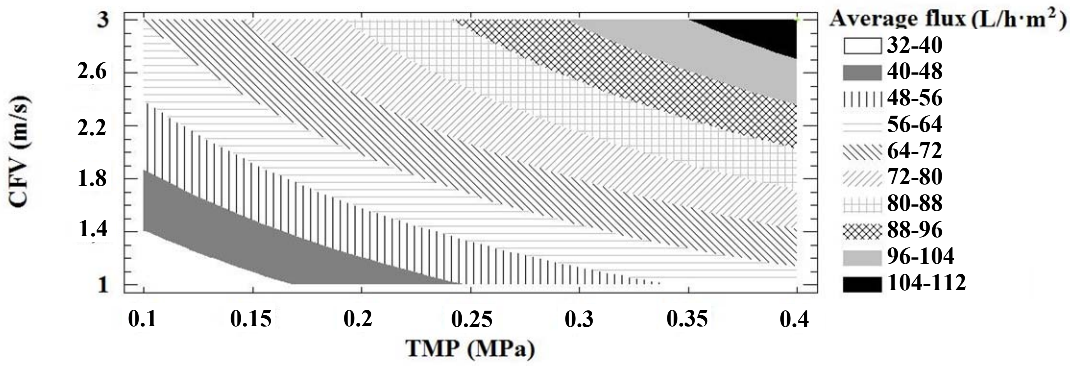

Fig. 6. Surface contours for average permeate flux for the Carbosep M2 membrane.

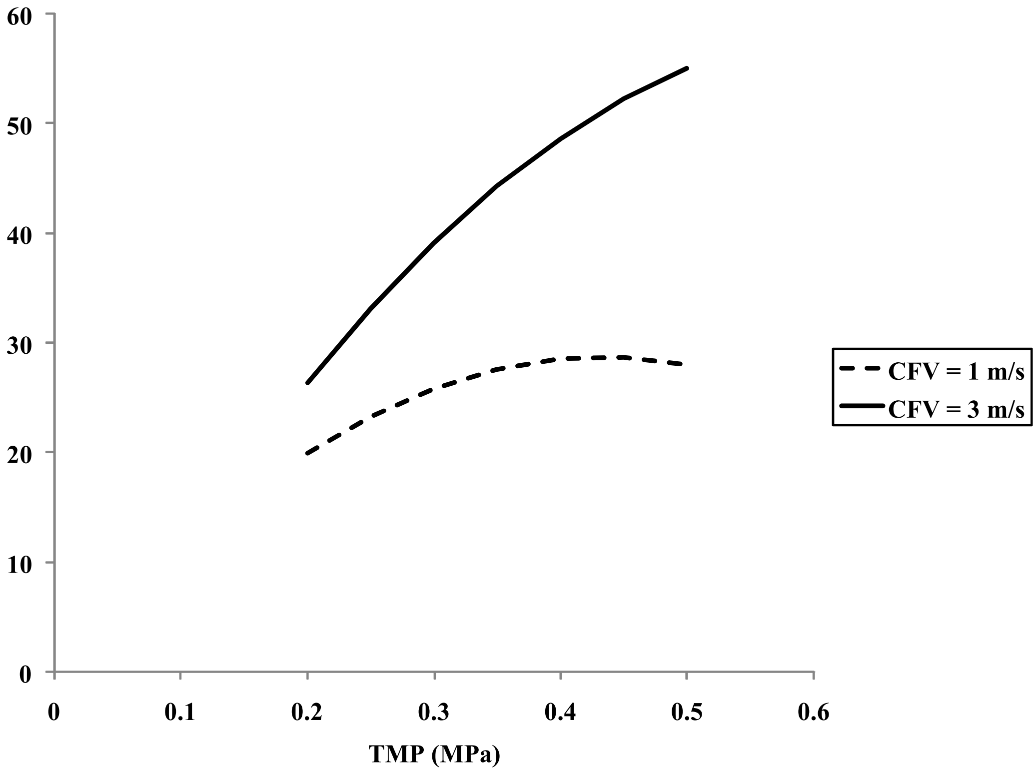

Fig. 7. Interaction plot of TMP and CFV for average permeate flux for the Tami MSKT membrane at a FC of 5 g/L.

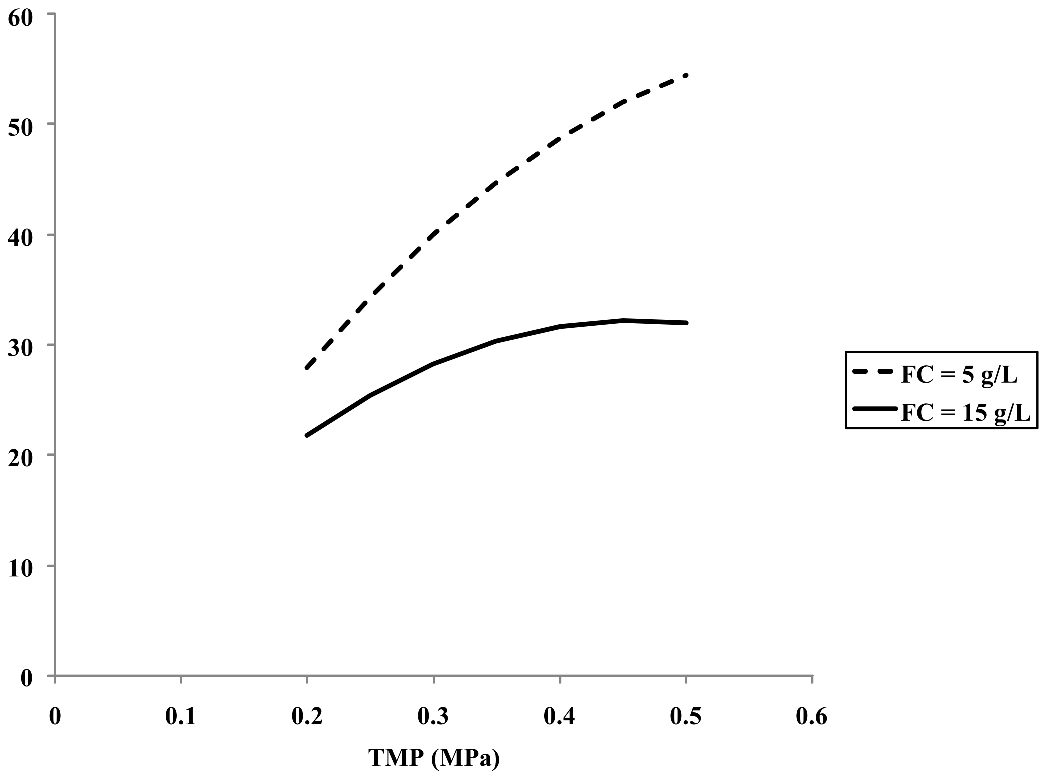

Fig. 8. Interaction plot of TMP and FC for average permeate flux for the Tami MSKT membrane at a CFV of 2 m/s.

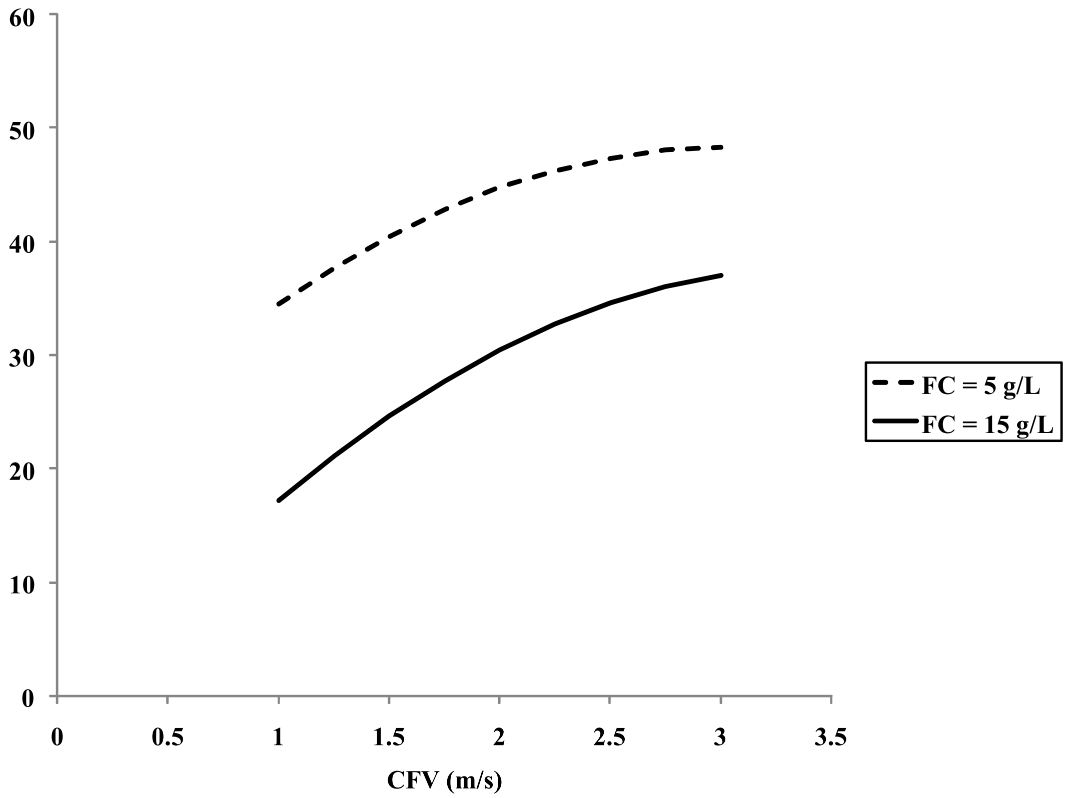

Fig. 9. Interaction plot of CFV and FC for average permeate flux for the Tami MSKT membrane at a TMP of 0.35 MPa.

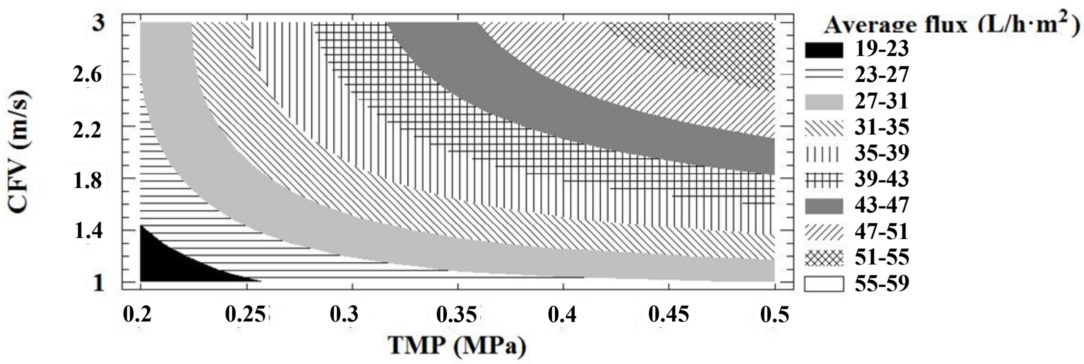

Fig. 10. Surface contours for estimated average permeate flux for the Tami MSKT membrane at medium values of feed concentration (10 g/L).

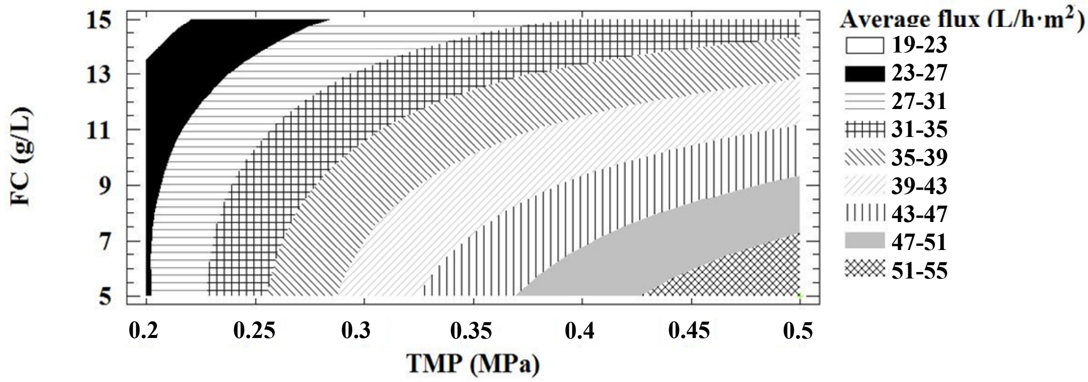

Fig. 11. Surface contours for estimated average permeate flux surface for the Tami MSKT membrane at medium values of crossflow velocity (2 m/s).

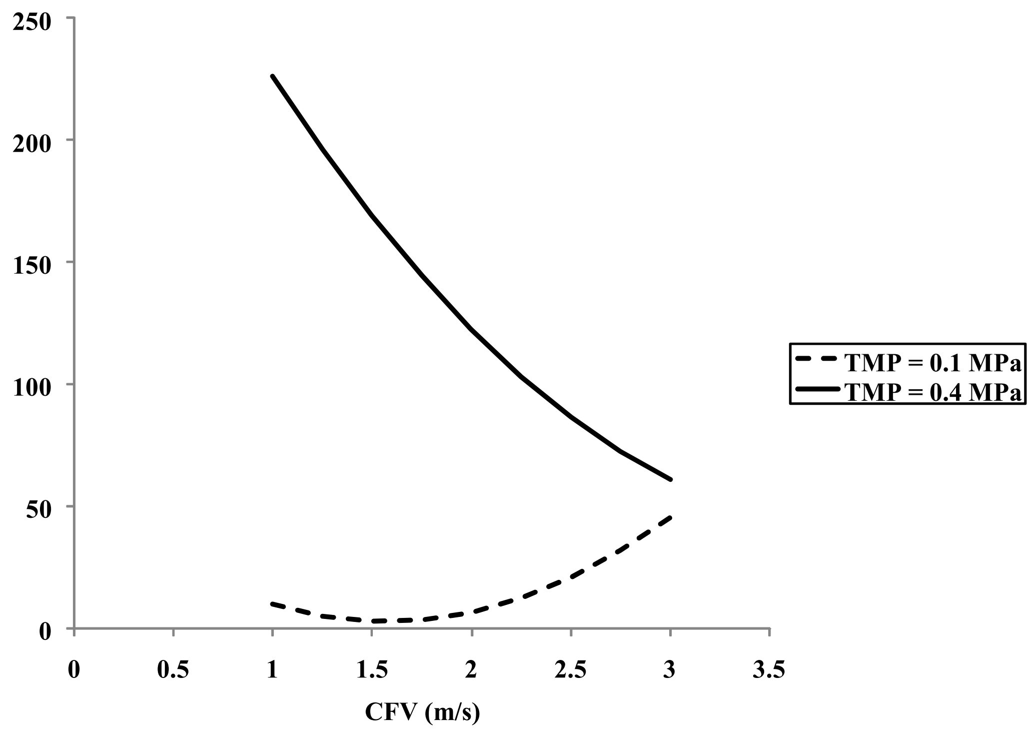

Fig. 12. Interaction plot for SFD for the Carbosep M2 membrane.

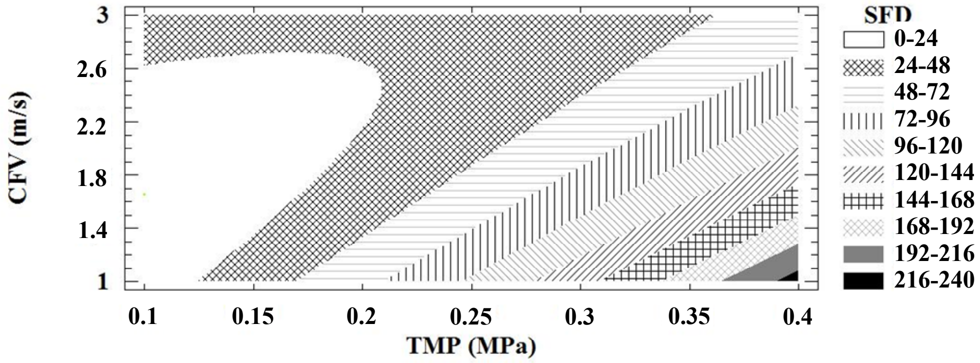

Fig. 13. Surface contours for SFD for the Carbosep M2 membrane.

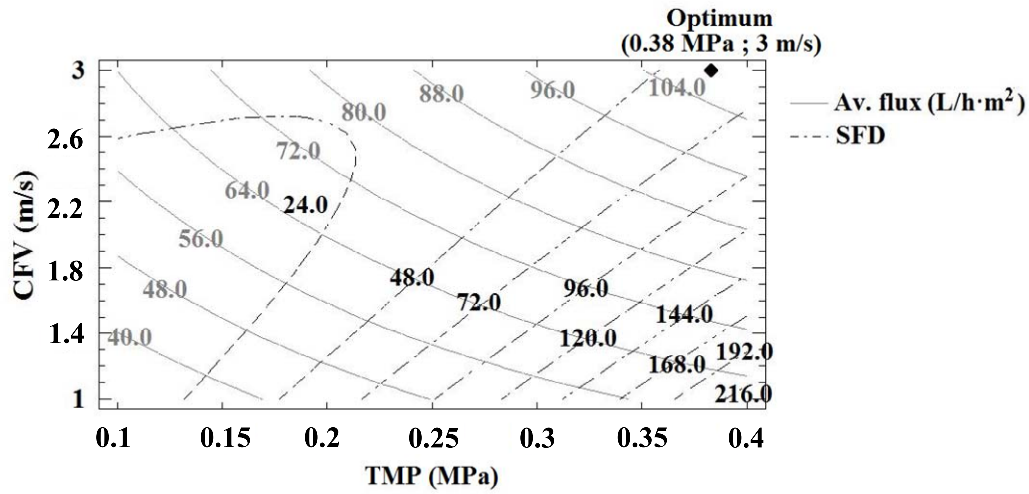

Fig. 14. Superimposed contour plots of the response variables as a function of TMP and CFV.