Salt cleaning of ultrafiltration membranes fouled by whey model solutions

María-José Corbatón-Báguena, Silvia Álvarez-Blanco*, María-Cinta Vincent-Vela

Department of Chemical and Nuclear Engineering, Universitat Politècnica de València, C/Camino de Vera s/n 46022 Valencia, Spain

*Corresponding author: sialvare@iqn.upv.es

Tel: +34963877000 (Ext.: 76383)

Fax: +34963877639 (Ext.: 77639)

Abstract

In this work, three ultrafiltration (UF) membranes were fouled with whey model solutions that contained BSA (1 % w/w) and $CaCl_2$ (0.06 % w/w). These membranes were cleaned with NaCl solutions. Temperature, crossflow velocity and concentration were varied. The membranes considered were a polyethersulfone (PES) membrane, a ceramic ZrO_2-TiO_2 membrane and a permanently hydrophilic polyethersulfone (PESH) membrane. Their molecular weight cut-offs (MWCOs) are 5, 15 and 30 kDa, respectively. The cleaning efficiency was related to the MWCO, membrane material and operating conditions. The results obtained demonstrated that NaCl solutions were able to clean the membranes tested. In addition, the higher the temperature and the crossflow velocity of the cleaning solution, the higher the cleaning efficiency was. However, there was an optimum value of NaCl concentration to clean the membranes effectively. When concentration was higher than the

optimum, the cleaning efficiency decreased. The relationship between the cleaning efficiency and the operating conditions was obtained with statistical and optimization analysis.

Keywords: Ultrafiltration; whey model solutions; NaCl solutions; membrane cleaning

1. Introduction

In dairy industries, ultrafiltration (UF) is one of the most widely used membrane separation processes. Its most important applications are milk dehydration, whey concentration and protein fractionation or purification [1, 2]. However, the major drawback in the application of UF processes is the progressive flux decline due to the fouling phenomena. In the dairy industry, membrane fouling is mainly caused by protein deposition on the membrane surface and adsorption inside its porous structure [3]. To minimize membrane fouling, several authors have investigated protein-protein, protein-membrane and also, protein-inorganic compounds interactions [3, 4, 5]. Almécija et al. [3] studied the influence of calcium salts on the UF of whey using a 50 kDa ceramic membrane. They demonstrated that these salts can act as binding agents between proteins. When the concentration of calcium salts increased, the percentage of membrane blocked pores during UF increased while the permeate flux through the membrane decreased. Ang and Elimelech [4] studied the effect of calcium concentration on the bovine serum albumin (BSA) fouling of reverse osmosis membranes. They reported that permeate flux decline was greater when calcium concentration increased, due to the reduction of the electrostatic repulsion among BSA molecules. Mo *et al.* [5] studied the effect of several cations and ionic strength on BSA fouling on reverse osmosis membranes. Calcium cations acted as crosslinking agents with

BSA molecules. Fouling experiments demonstrated that BSA fouling rate increased when calcium was present in the feed solution. Fouling rate also increased as ionic strength of the feed solution increased.

To overcome membrane fouling, membranes have to be cleaned to remove the deposits. In dairy industries, chemical cleaning procedures are carried out even twice a day [6]. The conventional procedure to clean membranes fouled with whey solutions consists of several steps of alkali, acid and disinfectant washings [1, 2, 3, 7]. However, membranes may be damaged by these cleaning agents, reducing the membrane lifetime and causing a negative impact on the environment when they are discharged as wastewaters. Therefore, alternative cleaning techniques have been developed in the last years such as electromagnetic fields [8], ultrasounds [9] and saline solutions. Several authors [10-12] have investigated the effect of salts on protein-protein interactions. Tsumoto et al. [10] studied the effect of several salts on protein-protein interactions. They observed that, at the same concentration, some salts (such as Na_2SO_4) caused a decline in protein solubility while other salts (such as NaCl) increased the solubility of proteins. The effect of salts that decreased protein solubility is known as salting-out effect. On the other hand, the effect of increasing protein solubility is known as salting-in effect. Zhang [11] reported that Cl^- was able to specifically bind to the proteins surface more strongly than other cations and anions. Thus, the repulsive intermolecular interactions increase and protein solubility also increases. Hofmeister [12] proposed a ranking of the capability of several cations and anions to salt-out or salt-in proteins. Based on the Hofmeister series, Nucci and Vanderkooi [13] reported a series of divalent and monovalent cations and classified them in order of their ability to precipitate proteins. According to these series, calcium cation is one of the most salting-out ions, which is in agreement with other works about the effect of calcium on protein fouling [3, 4].

However, only a few papers investigated membrane cleaning by means of saline solutions [14, 15]. Lee and Elimelech [14] cleaned reverse osmosis membranes fouled with alginate and calcium solutions with NaCl aqueous solutions at different concentrations. Their results showed that cleaning efficiencies of about 90 % were achieved with NaCl solutions of 50 mM. However, increasing NaCl concentration from 50 to 300 mM did not cause an increase in the cleaning efficiency. In a previous work, Corbatón-Báguena *et al.* [15] cleaned a 15 kDa MWCO UF membrane fouled with BSA solutions with different saline solutions (Na_2SO_4, NaCl, $NaNO_3$, NH_4Cl and KCl). The highest values of hydraulic cleaning efficiency (HCE) were obtained with NaCl, $NaNO_3$, NH_4Cl and KCl solutions.

The aim of this work is to evaluate the ability of NaCl solutions to clean a monotubular ceramic UF membrane of 15 kDa and two flat-sheet polymeric UF membranes of 5 and 30 kDa fouled by whey model solutions. The solutions consisted of BSA 1 % (w/w) and $CaCl_2$ (0.06 % (w/w) in calcium). The influence of the operating conditions (temperature, crossflow velocity and NaCl concentration of the cleaning solution), membrane material and molecular weight cut-off (MWCO) on the membrane cleaning efficiency was investigated. In order to determine the optimal values of the cleaning operating conditions to achieve the highest cleaning efficiency, statistical and optimization analysis were performed.

2. Materials and methods

2.1. Materials

Fouling experiments were performed using aqueous solutions that contained BSA (1 % (w/w)) and $CaCl_2$ (0.06 % (w/w) in calcium) as feed solutions. BSA (prepared by heat shock fractionation, lyophilized powder, 98 % purity, A3733, Sigma-Aldrich, Germany) and $CaCl_2$ (95 % purity, Panreac, Spain) were dissolved in deionized water until the above mentioned concentration was achieved. Isoelectric point of BSA is 4.9, according to the manufacturer. Feed solutions had a pH of about 7, thus BSA has mainly negative net charge on its surface. Its configuration is elliptic (11.6x2.7x2.7 nm) and it is one of the most widely used whey proteins to prepare model solutions for UF experiments [15, 16, 17, 18]. $CaCl_2$ is one of the most often used salts to study the interactions between whey proteins and salts [3, 4, 5].

Membranes were cleaned with NaCl aqueous solutions (121659, Panreac, Spain) at a pH ranging from 6.8 to 7. NaOH aqueous solutions (211687, Panreac, Spain) and NaClO aqueous solutions (211921, Panreac, Spain) at a pH 11 were used as alkaline cleaning agents.

2.2. Membranes

The membranes used in the experiments were: a flat sheet polyethersulfone (PES) membrane of 5 kDa (reference UP005), a flat sheet permanentely hydrophilic polyethersulfone (PESH) membrane of 30 kDa (reference UH030) and a monotubular ceramic membrane of 15 kDa. The polymeric membranes were supplied by Microdyn-Nadir, Germany. They had an effective area of 100 cm^2. The ceramic membrane was supplied by TAMI Industries, France. It consisted of a TiO_2 support layer and a ZrO_2-TiO_2 active layer and its effective area was 35.5 cm^2. It was 20 cm long with an internal diameter of 0.6 cm and an external diameter of 1 cm. The properties of these membranes are shown in Table 1. These membranes were selected for this study because their MWCO was lower than the molecular weight of BSA (67 kDa). This fact ensured high BSA rejection values. Moreover, they have MWCOs within the typical range for the production of whey protein concentrates. In addition, high thermal stability was desirable because high temperatures favour membrane cleaning. According to Table 1, this characteristic was common to all the membranes tested. Three different MWCOs (5, 15 and 30 kDa) and different membrane materials (PES, ZrO_2-TiO_2 and PESH) were selected to investigate their influence on the cleaning efficiency.

2.3. Experimental set-up

A VF-S11 UF plant (supplied by Orelis, France) was used to perform the fouling and cleaning experiments. It consisted of a 10 L stainless steel feed tank, a variable speed volumetric pump to control de crossflow velocity of each step, two manometers to measure the pressure drop across the membrane module, a temperature regulating system and a scale (0.001 g accuracy) to gravimetrically determine the permeate flux. This experimental set-up was described elsewhere [15].

All the experiments were performed in total recirculation mode, except in the case of the rinsing step. Operating conditions during the fouling experiments were a transmembrane pressure of 2 bar, a crossflow velocity of 2 $m \cdot s^{-1}$ and a temperature of 25 ºC. The duration of the tests was 3 h. These experimental conditions were selected according to previous studies on whey and protein ultrafiltration [15, 19].

2.4. Experimental procedure

2.4.1. Fouling experiments

Permeate flux, hydraulic resistance and rejection were measured during the fouling process to ensure that the values obtained were reproducible in all runs. Each fouling experiment was repeated a minimum of 10 times.

BSA rejection coefficient (Eq. 1) was calculated by measuring the permeate BSA concentration during the fouling tests. Measurements were performed by an UV-visible spectrophotometer (Hewlett-Packard 8453) at the wavelength corresponding with the maximum of BSA absorbance (278 mn).

$$\text{Rejection (\%)} = \left(1 - \frac{C_p}{C_b}\right) \cdot 100 \qquad \text{Eq. 1}$$

In Eq. 1 C_b is the BSA concentration in the feed solution (1 % (w/w)) and C_p is the permeate BSA concentration.

The hydraulic resistance (R) was determined by means of Darcy's law (Eq. 2) at the end of each fouling run.

$$J = \frac{\Delta P}{\mu \cdot R} \quad \text{Eq. 2}$$

where J is the permeate flux, ΔP is the transmembrane pressure, R is the total hydraulic resistance and μ is the feed solution viscosity.

2.4.2. Rinsing and cleaning experiments

After the fouling experiments, a washing step with deionized water prior to membrane cleaning (first rinsing) was performed to remove the reversible fouling from the membrane. Then, a cleaning step with NaCl solutions that allows the removal of the irreversible fouling was carried out. After the cleaning procedure, another rinsing step (second rinsing) with deionized water can be performed in order to remove the remaining loose foulant matter from the membrane surface and the cleaning agent molecules.

Cleaning experiments were performed at a transmembrane pressure of 1 bar, different crossflow velocities (1.2, 1.69, 2.18, 2.68, 3.19 and 4.2 $m \cdot s^{-1}$), five NaCl concentrations (0, 2.5, 5, 7.5 and 10 mM) and three temperatures (25, 37.5 and 50 º C). The pH of all the NaCl solutions ranged from 6.8 to 7. Each cleaning procedure was performed in duplicate. Before and after the cleaning step the membranes were rinsed at 25 ºC and the same transmembrane pressure and crossflow velocity as the cleaning step. During the rinsing and cleaning steps, low transmembrane pressure (1 bar) favours the relaxation of the compressible fouling layer formed in the fouling step and its removal [6].

The steps of cleaning and rinsing ended when the permeate flux and the hydraulic resistance of each step remained constant with time. The duration of the rinsing steps was 45 minutes, while the duration of the cleaning step ranged from 70 to 80 minutes.

After the last rinsing step, if the initial permeability conditions of the membranes were not recovered, membranes were cleaned with alkaline solutions. Polymeric membranes (5 and 30 kDa) were cleaned with NaOH aqueous solutions at 45 ºC and a pH of 11. The 15 kDa membrane was cleaned with 250 ppm NaClO aqueous solutions at a pH of 11. These cleaning procedures were recommended by the manufacturers to restore the membrane permselectivity properties.

2.5. Evaluation of membrane cleanliness

Daufin *et al.* [20] and Matzinos and Álvarez [19] developed a method to calculate the efficiency of rinsing and cleaning protocols. In these works, membranes were cleaned with NaOH solutions and the hydraulic resistance of the membrane after each step (fouling, first rinsing, cleaning and second rinsing) was determined by means of Darcy's law. These authors proposed an equation to evaluate the efficiency of the first rinsing to restore the membrane permeability. To evaluate the cleaning efficiency of the entire cleaning protocol to restore the initial membrane permeability, a similar equation (Eq. 3) was used [19, 20, 21]:

$$HCE = \frac{R_f - R_{r2}}{R_f - R_m} \cdot 100 \qquad \text{Eq. 3}$$

where *HCE* is the hydraulic cleaning efficiency, R_f is the fouling resistance, R_m is the resistance of the new membrane and R_{r2} is the hydraulic resistance after the second rinsing.

2.6. Statistical and optimization analysis

Results of the cleaning experiments were used to determine the relationship between the values of the cleaning operating conditions (temperature, T_c, NaCl concentration, C, and crossflow velocity, v) and the HCE by means of a Response Surface Methodology (RSM) analysis. This analysis was performed with the Statgraphics® software using a factorial design. After that, a Multiple Linear Regression analysis was carried out to obtain a model equation for HCE as a function of the operating conditions studied. In a first step, T_c, C, v and their interactions were considered. If a regression model coefficient had a p-value higher than 0.05, it was neglected because it was not statistically significant. Thus, a new regression analysis was performed until all the coefficients were statistically significant.

To determine the values of temperature, NaCl concentration and crossflow velocity that maximize the value of HCE for each membrane tested, an optimization method was performed with the model equations obtained in the RSM analysis. The optimization algorithm was based on the "patternsearch" function of Matlab® software, which finds the minimum of an objective function by means of a pattern search. Therefore, in this work the objective functions are the opposite functions of the model equations of HCE for each membrane. Additional parameters were included in the "patternsearch" function as the maximum value of temperature (50 ºC) and the maximum value of crossflow velocity (3.19 $m \cdot s^{-1}$ for the 5 and 30 kDa membranes and 4.2 $m \cdot s^{-1}$ for the 15 kDa membrane), as these were the higher values tested of these operating conditions.

2.7. AFM measurements

A Multimode Atomic Force Microscope (supplied by Veeco, Santa Barbara, CA, USA) with a NanoScope V controller was used to measure membranes roughness. Samples of 5 μm × 5 μm samples were used. Roughness was obtained by means of the tapping mode of imaging and the results were presented in terms of the Root Mean Square roughness (R_q). This parameter considers the standard deviation of the surface height values in a specific area (Eq. 4) [22]:

$$R_q = \sqrt{\frac{\sum\left(Z_i - Z_{avg}\right)^2}{N_p}} \qquad \text{Eq. 4}$$

In this equation, N_p is the number of points in the selected area, Z_i is the height value currently measured and Z_{avg} is the average of the height values.

3. Results and discussion

The values of R_m for the membranes used in the experiments were: $9.453\cdot10^{12}$, $5.001\cdot10^{12}$ and $3.794\cdot10^{12}$ m^{-1}, for the membranes of 5, 15 and 30 kDa, respectively. These values were taken as a reference to calculate HCE.

3.1. Fouling experiments

Evolution of permeate flux with time during the fouling step for the 5, 15 and 30 kDa membranes is shown in Fig. 1. Among all the membranes tested, the PESH 30 kDa membrane showed the lowest flux decline (19.96 %) during the fouling step in comparison with the PES 5 kDa membrane (34.62 %) and the ceramic 15 kDa membrane (39.82 %). The reason for that is the hydrophilic nature of the 30 kDa membrane. According to Rahimpour and Madaeni [23], the higher the hydrophilicity of the membrane surface is, the better the antifouling properties (high rejection coefficient, low permeate flux decline and low total filtration resistance) are. These authors tested the behavior of several PES membranes during the crossflow filtration of non-skim milk. Their results demonstrated that the hydrophilic PES membranes had a lower permeate flux decline (about 16 %) than the unmodified hydrophobic PES membrane (about 40 %). In addition, protein rejection was higher for the hydrophilic membranes than for the hydrophobic one. On the other hand, membrane fouling is also related to the surface roughness. When membrane roughness increases, fouling becomes more severe, because rougher surfaces favour the entrapment of foulant molecules [24]. This phenomenon can be observed for the membranes tested comparing permeate flux decline with the values of roughness (R_q) for each membrane tested. The highest flux decline was achieved for the 15 kDa membrane (R_q = 17.900 nm), followed by the 5 kDa membrane (R_q = 0.487 nm and hydrophobic) and the 30 kDa membrane (R_q = 1.657 nm and hydrophilic).

The variation of the rejection coefficient with time for the 5, 15 and 30 kDa membranes during the fouling step can be observed in Fig. 2. After 120 min of UF, BSA rejection was very similar for all the membranes tested (99.55 %, 99.64 % and 99.61% for the 5, 15 and 30 kDa membrane, respectively). These high rejection coefficients may be due to the great difference between the size of BSA molecules and the membrane pore size. When the foulant molecule size is much higher than the membrane pore size, these molecules can be retained on the membrane surface [25, 26].

Fig. 3 shows the evolution of the hydraulic resistance during the fouling, first rinsing, cleaning and second rinsing steps. The experimental conditions of transmembrane pressure, temperature and crossflow velocity were the same for all the membranes tested in the rinsing and cleaning steps: 1 bar, 2.18 $m \cdot s^{-1}$ and 25 ºC during the rinsing steps and 1 bar, 2.18 $m \cdot s^{-1}$ and 50 ºC in the cleaning step. However, NaCl concentration was higher for the polymeric membranes (7.5 mM) than in the case of the ceramic one (5 mM), because these were the values of NaCl concentration to obtain the highest HCE for each membrane at the experimental conditions above mentioned. According to Fig. 3, the HCE obtained for the 15 kDa membrane was the lowest (56.27 %), while the HCE for the 5 and 30 kDa membranes were higher than 90 % (90.98 % and 98.43 % , respectively). The reason for that is the higher roughness of the 15 kDa membrane compared with the 5 and 30 kDa membranes (R_q values of 0.487 and 1.657 nm, respectively). Therefore, higher values of crossflow velocity were tested for the 15 kDa membrane in order to achieve greater values of HCE.

3.2. Cleaning experiments

3.2.1. Influence of NaCl concentration

The effect of NaCl concentration on the values of HCE for each membrane was investigated. Several NaCl concentrations (0, 2.5, 5, 7.5, 10 and 12.5 mM) at two different temperatures (25 and 50 ºC) were considered. Crossflow velocity was set at 2.18 $m \cdot s^{-1}$ for the polymeric membranes (5 and 30 kDa) and at 4.2 m·s^{-1} for the 15 kDa membrane. Fig. 4 shows the results of the influence of NaCl concentration on the HCE. In the case of the polymeric membranes, HCE increased as NaCl concentration increased up to 7.5 mM for the two temperatures tested. However, above this salt concentration, HCE decreased (Figs. 4a and 4c). The same effect can be observed in Fig. 4b for the ceramic membrane: HCE increased as NaCl concentration increased up to 5 mM, but a higher increase in salt concentration caused a decrease in HCE for both temperatures studied. It can also be observed that, at the same experimental conditions (50 ºC and 7.5 mM of NaCl), the highest value of HCE was obtained for the 30 kDa membrane (98.42 %). The reason for this is the hydrophilic nature of the 30 kDa membrane as well as the small roughness that this membrane presents. Thus, this membrane showed less severe fouling than that of the 5 and 15 kDa membranes as it was already commented and it can be cleaned more easily [23].

Other authors [10, 14, 27] observed as well that there is an optimal value of the cleaning agents to clean different membranes. They reported that the cleaning efficiency increased as their concentration increased up to this optimal concentration. However, the cleaning efficiency did not increase or it could even decrease if the cleaning agent concentration increased above the optimal value. Lee and Elimelech [14] used NaCl solutions at different concentrations (0, 10, 25, 50, 100 and 300 mM) to clean reverse osmosis membranes fouled with alginate and calcium solutions. They achieved HCE values of about 90 % at a NaCl concentration of 50 mM. However, when NaCl concentration increased, the values of HCE remained constant. This may be due to the fact that the physical conditions for effective mass transfer were below the optimal ones [14]. Cabero Cabero [27] used conventional cleaning agents (alkaline and detergent aqueous solutions) to clean a ceramic

UF membrane fouled with whey protein concentrate solutions. This author reported that fouling and cleaning mechanisms may become competitive and that the cleaning agent molecules can be accumulated on the membrane surface or inside its pores. In addition, Tsumoto *et al.* [10] studied the effect of several salt concentrations on the surface tension. At low salt concentrations, the surface tension decreases as salt concentration increases, but the surface tension increases linearly with concentration at high salt concentrations. They also demonstrated that the salting-in effects of saline solutions are enhanced with a decrease in the surface tension. Thus, the salting-in effects of NaCl solutions are better observed at low salt concentrations.

3.2.2. Influence of cleaning solution temperature

Cleaning experiments were performed at three temperatures (25, 37.5 and 50 ºC) and two different NaCl concentrations and crossflow velocities (7.5 mM and 2.18 $m \cdot s^{-1}$ for the polymeric membranes and 5 mM and 4.2 $m \cdot s^{-1}$ for the ceramic membrane) to investigate the effect of the cleaning solution temperature on HCE for each membrane tested. The results obtained are shown in Fig. 5. As it can be observed, HCE increases as cleaning solution temperature increases for all the membranes tested. The highest HCE values (90.98 %, 99.05 % and 98.43 %) were achieved at the highest temperature tested (50 ºC) for the membranes of 5, 15 and 30 kDa respectively.

Some authors related the surface tension of a saline solution to the temperature [28, 29]. As temperature increases, the hydrophilic ions are adsorbed from the air/water surface and thus, the surface tension of the saline solution decreases [30]. As it was explained in section 3.2.1., the lower the surface tension is, the more enhanced the salting-in effects are

[10]. On the other hand, temperatures up to 50 ºC increase protein solubility and can weaken the structural stability of the fouling layer, swelling it and favouring its removal from the membrane surface [31]. The rate of foulant molecules transferred from the membrane surface to the feed solution also increases when the cleaning solution temperature increases, due to the increase in the diffusivity coefficient as temperature rises. Moreover, the rate of the interaction between the salt and the deposited proteins may be increased by an increase in temperature [14].

For all these reasons, the highest temperature tested (50 ºC) is the most convenient temperature to perform the cleaning process when the membranes are fouled with BSA and $CaCl_2$ solutions.

3.2.3. Influence of crossflow velocity

Fig. 6 shows the variation of HCE with crossflow velocity for all the membranes tested. The values of NaCl concentration and temperature that were selected to study the influence of the crossflow velocity on HCE were the ones at which the highest values of HCE were obtained. These conditions were a NaCl concentration of 7.5 mM and 50 ºC for the polymeric membranes and a NaCl concentration of 5 mM and 50 ºC for the ceramic membrane. In the case of the 5 and 30 kDa membranes (Fig. 6a), lower values of crossflow velocity were tested (1.2 and 1.69 $m \cdot s^{-1}$), due to the lower roughness of these membranes compared with the ceramic one.

The Fig. 6 shows that when crossflow velocity increases, HCE increases. For all the membranes tested, values of HCE near 100 % were achieved at the highest crossflow velocity tested (3.19 $m \cdot s^{-1}$ for the 5 and 30 kDa membranes and 4.2 $m \cdot s^{-1}$ for the 15 kDa membrane). As the crossflow velocity increases, the shear force increases as well favouring the removal of foulant molecules from the membrane surface [32, 33, 34].

3.3. Statistical and optimization analysis

The influence of the operating conditions (temperature, NaCl concentration and crossflow velocity) on the values of HCE was evaluated by means of statistical (RSM and Multiple Linear Regression) and optimization (pattern search algorithm) analysis.

The effect of temperature and NaCl concentration on HCE for the 5, 15 and 30 kDa membranes is shown in Fig. 7. Light grey and white colours in the lower left corner of the surface contours represented the most unfavourable conditions to perform the cleaning procedure. These conditions corresponded to the lowest temperature (25 ºC) and NaCl concentration (0 mM) tested. On the other hand, the highest values of HCE (higher than 90 %) were achieved at temperatures higher than 46-50 ºC and NaCl concentrations ranging from 7.5 to 10 mM for the 5 and 30 kDa membranes and from 4.5 to 5 mM in the case of the 15 kDa membrane. These experimental conditions are coloured in black in Fig. 7.

After the RSM analysis, a Multiple Linear Regression was performed to relate HCE with temperature, NaCl concentration and crossflow velocity. Eqs. 5, 6 and 7 show these mathematical relationships for the 5, 15 and 30 kDa membranes, respectively. The regression coefficients for each equation were 0.976, 0.970 and 0.962, respectively. Table 2 shows the results of the ANOVA.

$$\mathrm{HCE}_5\ (\%) = \mathrm{a} + \mathrm{b}\cdot v + \mathrm{c}\cdot T_c\cdot C + \mathrm{d}\cdot T_c^2 + \mathrm{e}\cdot C^2 + \mathrm{f}\cdot v^2 \qquad \text{Eq. 5}$$

$$\mathrm{HCE}_{15}\ (\%) = \mathrm{a} + \mathrm{g}\cdot T_c + \mathrm{c}\cdot T_c\cdot C + \mathrm{e}\cdot C^2 + \mathrm{f}\cdot v^2 \qquad \text{Eq. 6}$$

$$\mathrm{HCE}_{30}\ (\%) = \mathrm{a} + \mathrm{h}\cdot C + \mathrm{b}\cdot v + \mathrm{d}\cdot T_c^2 + \mathrm{e}\cdot C^2 + \mathrm{f}\cdot v^2 \qquad \text{Eq. 7}$$

In these equations, HCE_5, HCE_{15} and HCE_{30} are the hydraulic cleaning efficiencies for the membranes of 5, 15 and 30 kDa, respectively, T_c is the temperature of the cleaning solution (ºC), C is the NaCl concentration (mM), v is the crossflow velocity ($\mathrm{m\cdot s^{-1}}$) and a, b, c, d, e, f, g and h are the estimated coefficients for each statistically significant parameter. Their estimated values are shown in Table 2.

The values of the coefficients of the significant parameters are in agreement with the experimental observations. Within the range of values of the operating parameters considered in this work, the equations for the polymeric membranes predicted that HCE increases with v and decreases with v^2. The values of the coefficients indicate that the increase in HCE with this variable was much more significant at low values of v, while at the largest values of v the increase in HCE was much lower. However, in the case of the ceramic membrane HCE was highly affected by v and linearly increased with this variable for all the operating conditions tested, probably due to the greater roughness of this membrane. The model equations predicted as well that HCE was highly affected by T_c and it significantly increased with this variable for all the membranes. Regarding the effect of NaCl concentration on HCE, the model equations predicted that HCE increased with C and decreased with C^2. This indicates that at low values of NaCl concentration HCE increases with this variable up to an optimum concentration and a further increase in NaCl concentration caused a decrease in HCE. For some of the membranes there was an interaction between concentration and temperature, which indicates that the effect of concentration on HCE is greater at higher NaCl concentrations and vice versa.

Results of the optimization analysis based on the “patternsearch” function of Matlab® are shown in Table 3. According to them, the optimal cleaning solution temperature was 50 ºC for all the membranes tested. Optimal values of crossflow velocity and NaCl concentration were: 3.15 $m \cdot s^{-1}$ and 10 mM for the 5 kDa membrane, 4.2 $m \cdot s^{-1}$ and 7.17 mM for the 15 kDa membrane and 2.82 $m \cdot s^{-1}$ and 9.76 mM for the 30 kDa membrane.

4. Conclusions

- Three different ultrafiltration membranes of 5, 15 and 30 kDa that had been previously fouled with whey model solutions consisting of BSA (1 % w/w) and $CaCl_2$ (0.06 % w/w in calcium) were effectively cleaned with NaCl solutions. NaCl was effective as a cleaning agent at the experimental conditions tested due to the salting-in effect of this salt.

- An increase in temperature and crossflow velocity resulted in an increase in HCE.

- There was an optimal value of NaCl concentration to clean the membranes. If NaCl concentration increased up to this optimal value, HCE increased; but a further increase in NaCl concentration caused a decrease in the values of HCE.

- The optimal operating conditions that resulted in the maximum values of HCE (about 100 %) were: a temperature of 50 ºC for all the membranes, a crossflow velocity of 3.15 $m \cdot s^{-1}$ and a NaCl concentration of 10 mM for the 5 kDa membrane, a crossflow velocity of 4.2 $m \cdot s^{-1}$ and NaCl concentration of 7.17 mM for the 15 kDa membrane and a crossflow velocity of 2.82 $m \cdot s^{-1}$ and a NaCl concentration of 9.76 mM for the 30 kDa membrane.

- Mathematical relationships between HCE and the operating conditions were determined for all the membranes considered using a multiple linear regression analysis.

Acknowledgements

The authors of this work wish to gratefully acknowledge the financial support from the Spanish Ministry of Science and Innovation through the project CTM2010-20186 and the Generalitat Valenciana through the program "Ayudas para la realización de proyectos I+D para grupos de investigación emergentes GV/2013".

Nomenclature

List of symbols

a	Model equation coefficient (%)
b	Model equation coefficient ($m^{-1} \cdot s$)
c	Model equation coefficient ($ºC^{-1} \cdot mM^{-1}$)

C	NaCl concentration (mM)
C_b	BSA concentration in the feed solution ($g \cdot L^{-1}$)
C_p	BSA concentration in the permeate ($g \cdot L^{-1}$)
d	Model equation coefficient ($ºC^{-2}$)
e	Model equation coefficient (mM^{-2})
f	Model equation coefficient ($m^{-2} \cdot s^{2}$)
g	Model equation coefficient ($ºC^{-1}$)
h	Model equation coefficient (mM^{-1})
J	Permeate flux ($m^{3} \cdot m^{-2} \cdot s^{-1}$)
N_p	Number of points within the given area (dimensionless)
ΔP	Transmembrane pressure (bar)
R	Total hydraulic resistance (m^{-1})
R_m	Resistance of the new membrane (m^{-1})
R_f	Resistance after the fouling step (m^{-1})
R_{r1}	Resistance after the first rinsing step (m^{-1})
R_c	Resistance after the cleaning step (m^{-1})
R_{r2}	Resistance after the second rinsing step (m^{-1})
t	Filtration time (s)
T_c	Temperature of the cleaning solution (ºC)
v	Crossflow velocity ($m \cdot s^{-1}$)
Z_i	Value of height currently measured (nm)
Z_{avg}	Average of the height values of the sample (nm)

Greek letters

μ Feed solution viscosity ($kg \cdot m^{-1} \cdot s^{-1}$)

Abbreviations

AFM	Atomic force microscopy
BSA	Bovine serum albumin
HCE	Hydraulic cleaning efficiency
HRE	Hydraulic rinsing efficiency
MWCO	Molecular weight cut off
PES	Polyethersulfone
pI	Isoelectric point
RSM	Response surface methodology
UF	Ultrafiltration

References

[1] O.O. Ogunbiyi, N.J. Miles, N. Hilal, The effects of performance and cleaning cycles of new tubular ceramic microfiltration membrane fouled with a model yeast suspension, Desalination 220 (2008) 273-289.

[2] M. Kazemimoghadam, T. Mohammadi, Chemical cleaning of ultrafiltration membranes in the milk industry, Desalination 204 (2007) 213-218.

[3] M.C. Almécija, A. Martínez-Férez, A. Guadix, M.P. Páez, E.M. Guadix, Influence of the cleaning temperature on the permeability of ceramic membranes, Desalination 245 (2009) 708-713.

[4] W.S. Ang, M. Elimelech, Protein (BSA) fouling of reverse osmosis membranes: Implications for wastewater reclamation, J. Membr. Sci. 296 (2007) 83-92.

[5] H. Mo, K.G. Tay, H.Y. Ng, Fouling of reverse osmosis membrane by protein (BSA): Effects of pH, calcium, magnesium, ionic strength and temperature, J. Membr. Sci. 315 (2008) 28-35.

[6] P. Blanpain-Avet, J.F. Migdal, T. Bénézech, Chemical cleaning of a tubular ceramic microfiltration membrane fouled with a whey protein concentrate suspension-Characterization of hydraulic and chemical cleanliness, J. Membr. Sci. 337 (2009) 153-174.

[7] M.C. Almécija, J.E. Zapata, A. Martínez-Férez, A. Guadix, A. Hernández, J.I. Calvo, E.M. Guadix, Analysis of cleaning protocols in ceramic membranes by liquid-liquid displacement porosimetry, Desalination 245 (2009) 541-545.

[8] C.C. Taragaza, M.E. Campderrós, A. Pérez Padilla, Physical cleaning by means of electric field in the ultrafiltration of a biological solution, J. Membr. Sci. 278 (2006) 219-224.

[9] S. Muthukumaran, K. Yang, A. Seuren, S. Kentish, M. Ashokkumar, G.W. Stevens, R. Grieser, The use of ultrasonic cleaning for ultrafiltration membranes in the dairy industry, Sep. Purif. Technol. 39 (2004) 99-107.

[10] K. Tsumoto, D. Ejima, A.M. Senczuk, Y. Kita, T. Arakawa, Effects of salts on protein-surface interactions: Applications for column chromatography, J. Pharmaceutical Sci. 96 (2007) 1677-1690.

[11] J. Zhang, Chapter 18: Protein-protein interactions in salt solutions, in: W. Cai, H. Hong (Eds.) Protein-protein interactions – Computational and experimental tools, Intech, 2012, pp. 359- 376.

[12] F. Hofmeister, Zur lehre von der wirkung der salze, Arch. Exp. Pathol. Pharmakol. 24 (1888) 247.

[13] N.V. Nucci, J.M. Vanderkooi, Effects of salts of the Hofmeister series on the hydrogen bond network of water, J. Mol. Liq. 143 (2008) 160-170.

[14] S. Lee, M. Elimelech, Salt cleaning of organic-fouled reverse osmosis membranes, Water Res. 41 (2007) 1134-1142.

[15] M-J. Corbatón-Báguena, S. Álvarez-Blanco, M-C. Vincent-Vela, Cleaning of ultrafiltration membranes fouled with BSA by means of saline solutions, Sep. Purif. Technol. 125 (2014) 1-10.

[16] P. Suttiprasit, V. Krisdhasima, J. McGuire, The surface activity of α-lactalbumin, β-lactoglobulin and bovine serum albumin, J. Colloid Interface Sci., 154 (1992) 316-326.

[17] Y-N. Wang, C.Y. Tang, Protein fouling of nanofiltration, reverse osmosis, and ultrafiltration membranes-The role of hydrodynamic conditions, solution chemistry and membrane properties, J. Membr. Sci. 376 (2011) 275-282.

[18] A. Afonso, J.M. Miranda, J.B.L.M. Campos, Numerical study of BSA ultrafiltration in the limiting flux regime – Effect of variable physical properties, Desalination 249 (2009) 1139-1150.

[19] P. Matzinos, R. Álvarez, Effect of ionic strength on rinsing and alkaline cleaning of ultrafiltration inorganic membranes fouled with whey proteins, J. Membr. Sci. 208 (2002) 23-30.

[20] G. Daufin, J.-P. Escudier, H. Carrère, S. Bérot, L. Fillaudeau, M. Decloux, Recent and emerging applications of membrane processes in the food and dairy industry, Food Bioprod. Process. 79 (2001) 89-102.

[21] S. Muthukumaran, S.E. Kentish, G.W. Stevens, M. Ashokkumar, R. Mawson, The application of ultrasound to dairy ultrafiltration: The influence of operating conditions, J. Food Eng. 81 (2007) 364-373.

[22] T.-S. Chung, J.-J. Qin, A. Huan, K.-C. Toh, Visualization of the effect of die shear rate on the outer surface morphology of ultrafiltration membranes by AFM, J. Membr. Sci. 196 (2002) 251–266.

[23] A. Rahimpour, S.S. Madaeni, Improvement of performance and surface properties of nano-porous polyethersulfone (PES) membrane using hydrophilic monomers as additives in the casting solution, J. Membr. Sci. 360 (2010) 371-379.

[24] P.J. Evans, M.R. Bird, A. Pihlajamäki, M. Nyström, The influence of hydrophobicity, roughness and charge upon ultrafiltration membranes for black tea liquor clarification, J. Membr. Sci. 313 (2008) 250-262.

[25] A.I. Schäfer, A.G. Fane, T.D. Waite, Fouling effects on rejection in the membrane filtration of natural waters, Desalination 131 (2000) 215-224.

[26] H.V. Adikane, D.M. Thakar, S.N. Nene, Optimisation of colour and sugar rejection of black liquior using membranes, Sep. Purif. Technol. 36 (2004) 229-234.

[27] M.L. Cabero Cabero, Limpieza química de membranas inorgánicas: Aplicación al tratamiento de lactosuero, PhD Thesis, University of Oviedo, 1997.

[28] K. Ali, A-u-H.A. Shah, S. Bilal, Thermodynamic parameters of surface formation of some aqueous salt solutions, Colloids and Surfaces A: Physicochem. Eng. Aspects, 330 (2008) 28-34.

[29] A-u-H.A. Shah, K. Ali, S. Bilal, Surface tension, surface excess concentration, enthalpy and entropy of surface formation of aqueous salt solutions. Colloids and Surfaces A: Physicochem. Eng. Aspects, 417 (2013) 183-190.

[30] N. Matubayasi, R. Yoshikawa, Thermodynamic quantities of surface formation of aqueous electrolyte solutions VII. Aqueous solution of alkali metal nitrates $LiNO_3$, $NaNO_3$ and KNO_3, J. Colloid Interface Sci., 315 (2007) 597-600.

[31] D.H.G. Pelegrine, C.A. Gasparetto, Whey proteins solubility as function of temperature and pH, Lebensm.-Wiss. u.-Technol, 38 (2005) 77-80.

[32] Ü. Daniş, B. Keskinler, Chromate removal from wastewater using micellar enhanced crossflow filtration: Effect of transmembrane pressure and crossflow velocity, Desalination, 249 (2009) 1356-1364.

[33] P.J. Smith, H.K. Shon, S. Vigneswaran, H.H. Ngo, H. Nguyen, Productivity enhancement in a cross-flow ultrafiltration membrane system through automated de-clogging operations, J. Membr. Sci., 280 (2006) 82-88.

[34] H. Choi, K. Zhang, D.D. Dionysiou, D.B. Oerther, G.A. Sorial, Influence of cross-flow velocity on membrane performance during filtration of biological suspension, J. Membr. Sci. 248 (2005) 189-199.

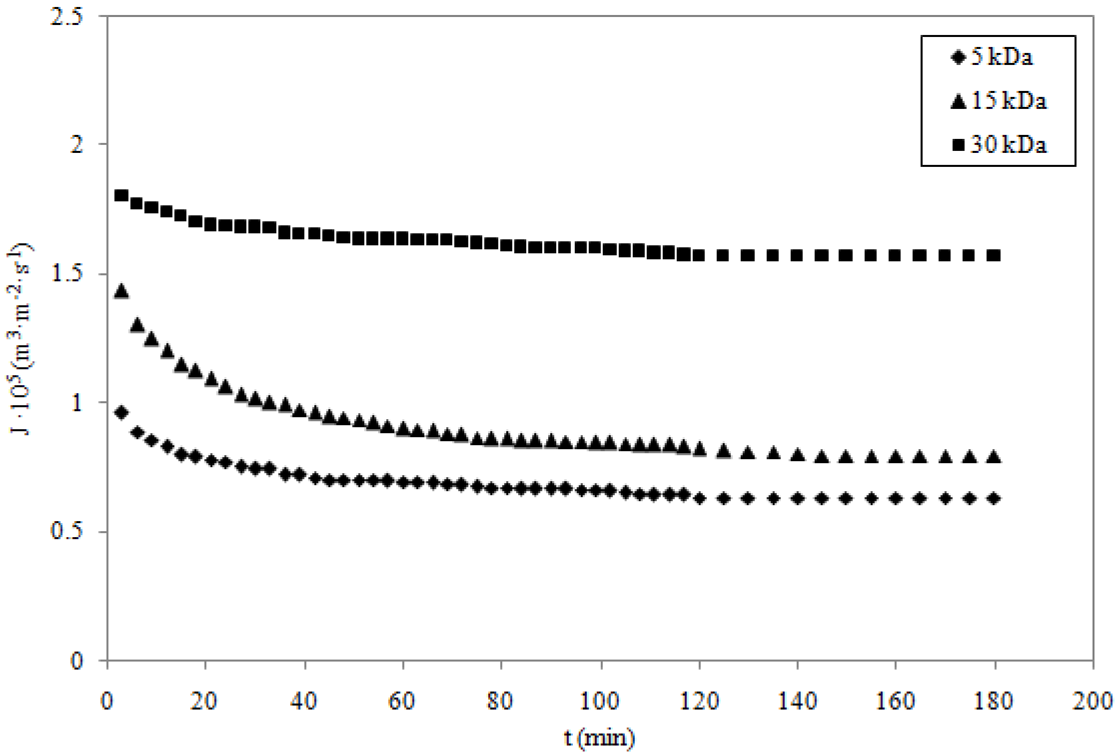


Fig. 1. Variation of permeate flux with time during fouling experiments at 2 bar, 2 $m \cdot s^{-1}$ and 25 ºC.

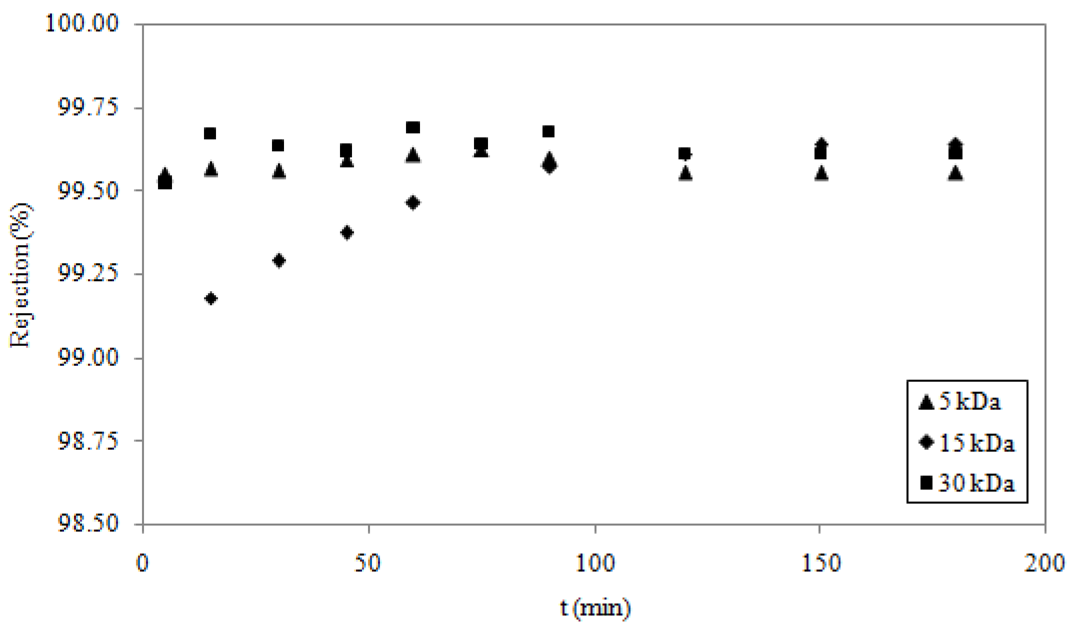


Fig. 2. Variation of BSA rejection with time during the fouling step for each membrane.

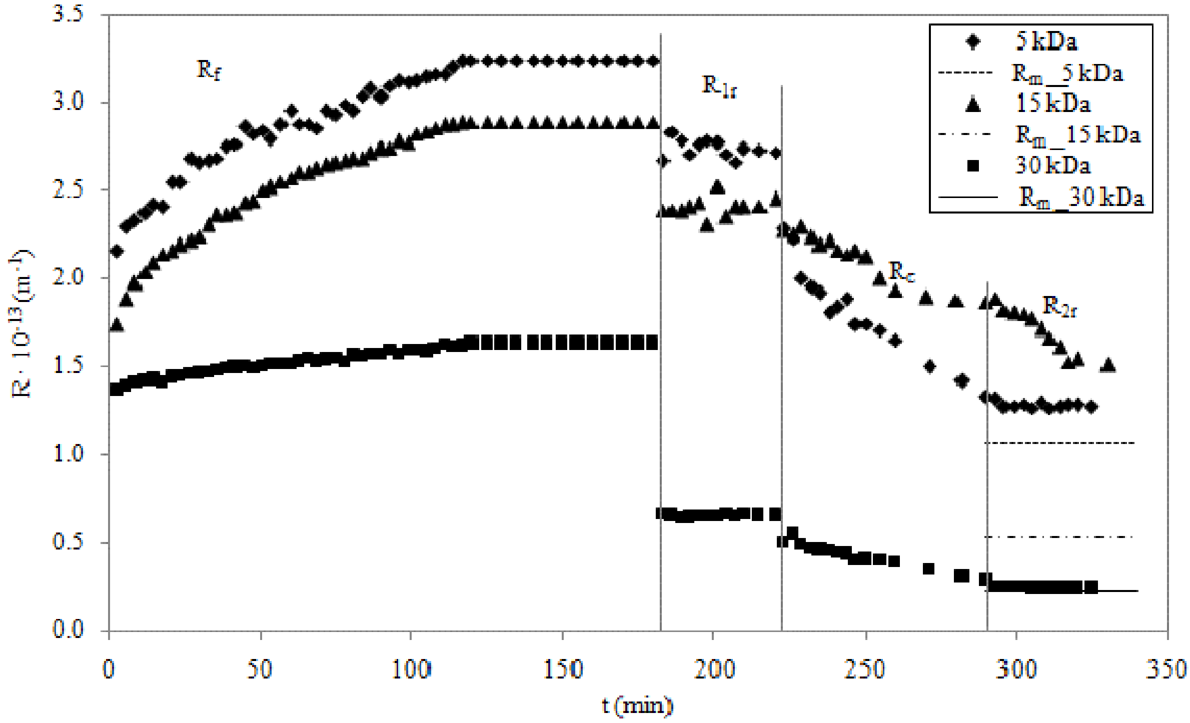


Fig. 3. Variation of total hydraulic resistance with time for each membrane when the experimental conditions were: 25 ºC, 2 bar and 2 m·s^{-1} in the fouling step; 25 ºC, 1 bar and 2.18 m·s^{-1} in the rinsing steps; 50 ºC, 1 bar and 2.18 m·s^{-1} in the cleaning step. NaCl concentration in the cleaning solution was 7.5 mM for the 5 and 30 kDa membranes and 5 mM for the 15 kDa membrane.

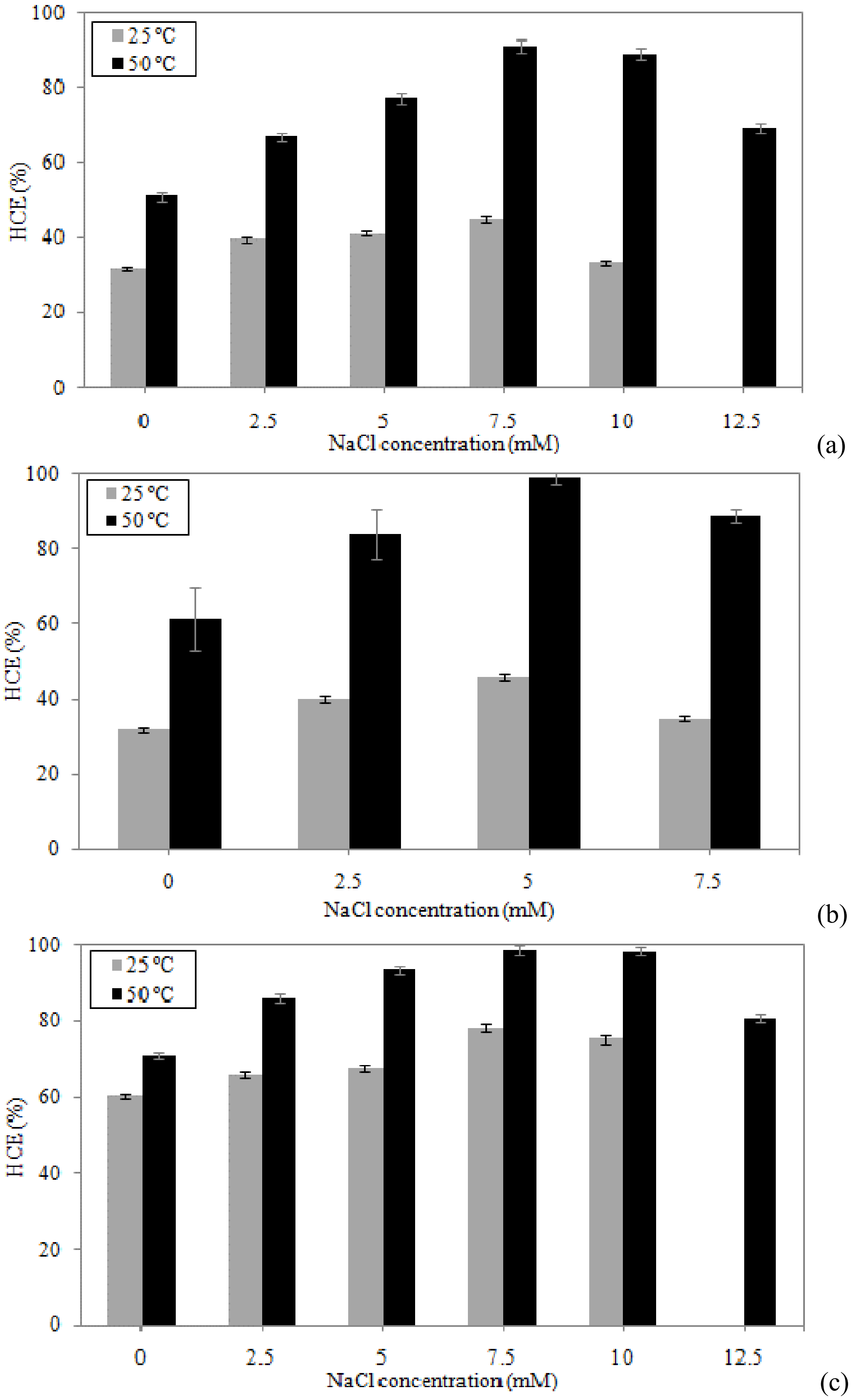
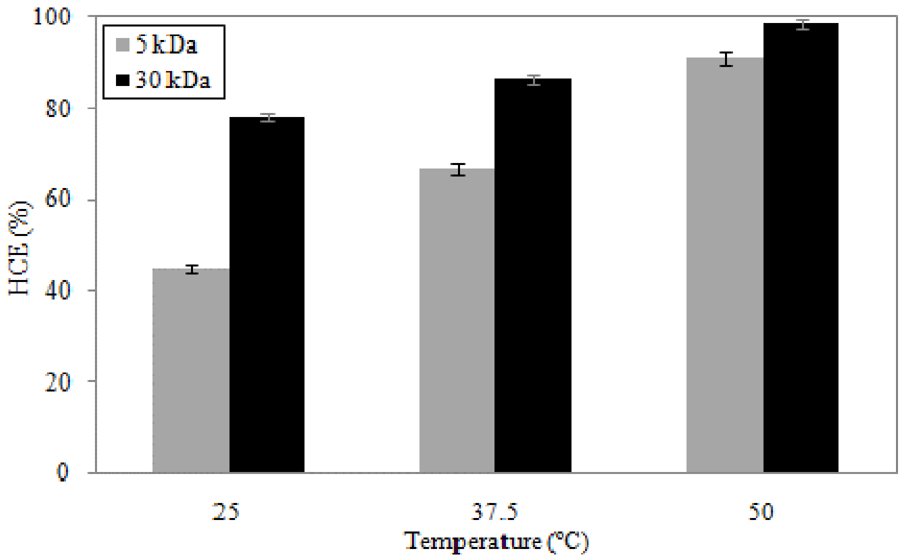
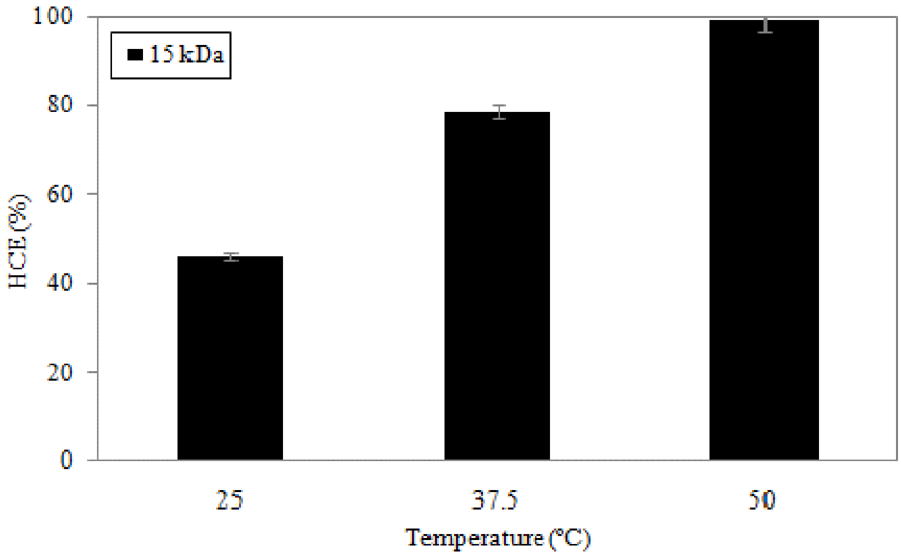


Fig. 4. Influence of NaCl concentration on the values of HCE for the membranes of 5 kDa (a), 15 kDa (b) and 30 kDa (c), when the cleaning solution temperature is 25 ºC (grey bars) and 50 ºC (black bars) and the crossflow velocity is 2.18 $m \cdot s^{-1}$ for the polymeric membranes and 4.2 $m \cdot s^{-1}$ for the ceramic membrane.



(a)



(b)

Fig. 5. Influence of temperature on the values of HCE for the membranes of: (a) 5 kDa (grey bars) and 30 kDa (black bars) at 2.18 $m \cdot s^{-1}$ and a NaCl concentration of 7.5 mM, and (b) 15 kDa at 4.2 $m \cdot s^{-1}$ and a NaCl concentration of 5 mM.

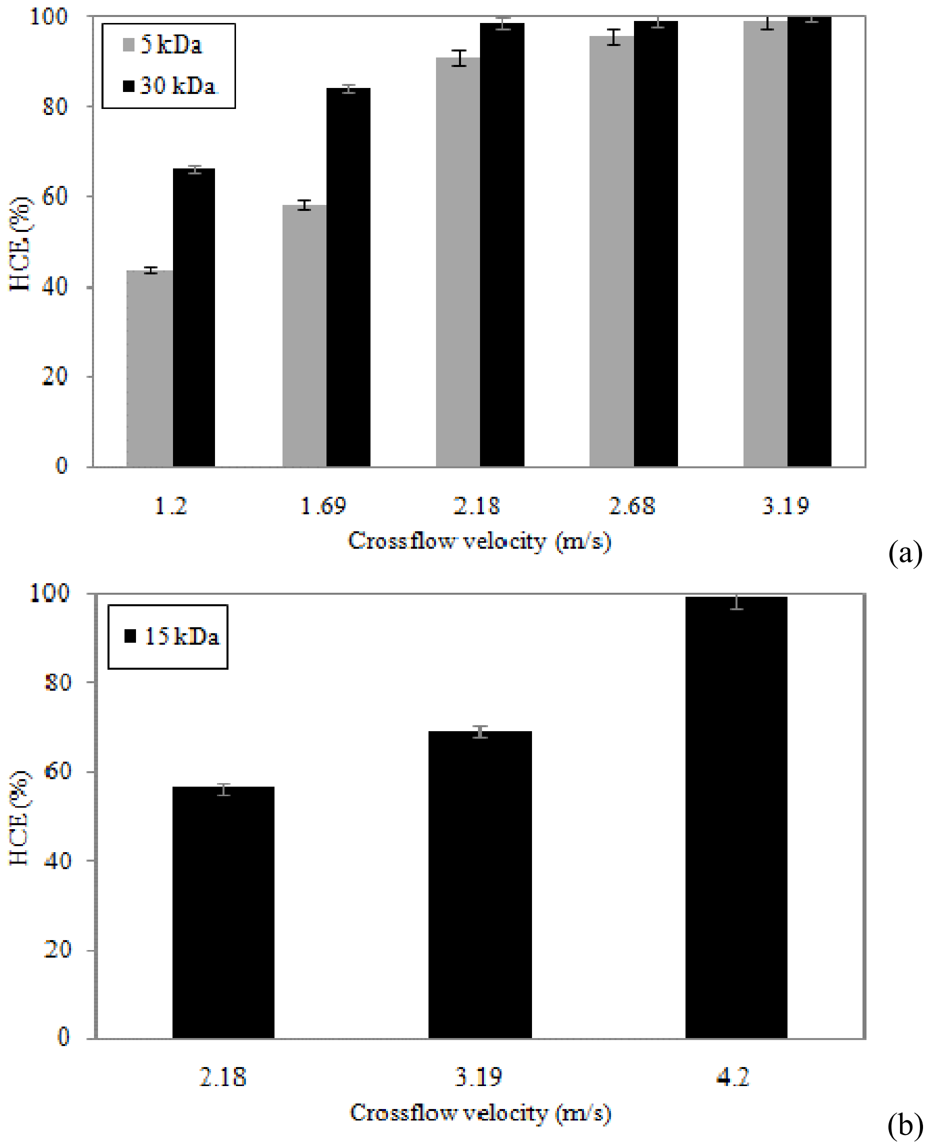


Fig. 6. Influence of crossflow velocity on the values of HCE for the membranes of: (a) 5 kDa (grey bars) and 30 kDa (black bars) at 50 ºC and a NaCl concentration of 7.5 mM, and (b) 15 kDa at 50 ºC and a NaCl concentration of 5 mM.

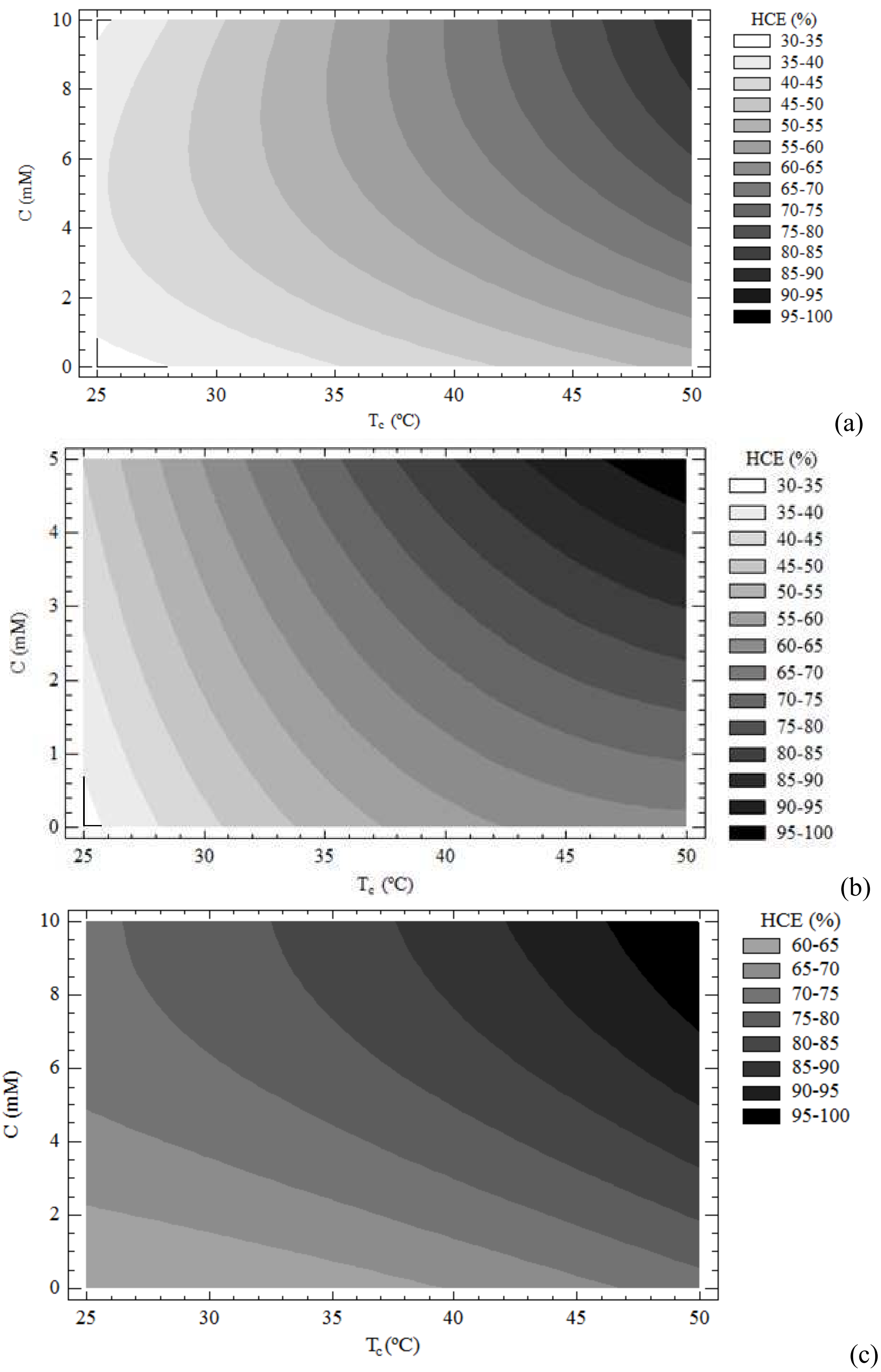


Fig. 7. Contour plot for HCE as a function of temperature and NaCl concentration for the membranes of 5 kDa (a), 15 kDa (b) and 30 kDa (c) at a crossflow velocity of 2.18 $m \cdot s^{-1}$ for the polymeric membranes and 4.2 $m \cdot s^{-1}$ for the ceramic membrane.

Table 1
Main properties of the membranes used.

Item	UP005	INSIDE-CERAM^{TM}	UH030
Manufacturer	Microdyn Nadir	TAMI Industries	Microdyn Nadir
Type	Flat-sheet	Tubular	Flat-sheet
MWCO (kDa)	5	15	30
Active layer	PES	ZrO_2-TiO_2	PESH
Effective area (cm^2)	100.00	35.51	100.00
Water permeability 25ºC ($L·m^{-2}h^{-1}·bar^{-1}$)	42.61	60.37	106.17
Maximum operating temperature (ºC)	95	95	95
pH range	0-14	0-14	0-14

Table 2
ANOVA results for the model equations that relate HCE with the operating parameters.

MWCO (kDa)	Parameter	Coefficient	Estimated value	p-value
5	Constant	a (%)	-112.043	0.0000
	v	b ($m^{-1}·s$)	97.093	0.0000
	$T_c·C$	c ($ºC^{-1}·mM^{-1}$)	0.134	0.0000
	T_c^2	d ($ºC^{-2}$)	0.010	0.0001
	C^2	e (mM^{-2})	-0.299	0.0010
	v^2	f ($m^{-2}·s^2$)	-15.391	0.0007
15	Constant	a (%)	-43.946	0.0024
	T_c	g ($ºC^{-1}$)	1.088	0.0006
	$T_c·C$	c ($ºC^{-1}·mM^{-1}$)	0.187	0.0010
	C^2	e (mM^{-2})	-0.653	0.0054
	v^2	f ($m^{-2}·s^2$)	2.968	0.0001
30	Constant	a (%)	-50.809	0.0029
	C	h (mM^{-1})	4.322	0.0001
	v	b ($m^{-1}·s$)	75.194	0.0000
	T_c^2	d ($ºC^{-2}$)	0.011	0.0000
	C^2	e (mM^{-2})	-0.221	0.0095
	v^2	f ($m^{-2}·s^2$)	-13.333	0.0002

Table 3
Optimal values of the operating parameters obtained by means of a pattern-search algorithm.

MWCO (kDa)	T_c (ºC)	C (mM)	v ($m·s^{-1}$)
5	50	10.00	3.15
15	50	7.17	4.20
30	50	9.76	2.82