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Utilization of NaCl solutions to clean ultrafiltration membranes fouled by whey protein concentrates

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Abstract

In this work, whey protein concentrate (WPC) solutions at different concentrations (22.2, 33.3 and 150 g·L^{-1}) were used to foul three ultrafiltration (UF) membranes of different materials and molecular weight cut-offs (MWCOs): a polyethersulfone (PES) membrane of 5 kDa, a ceramic ZrO_2-TiO_2 membrane of 15 kDa and a permanently hydrophilic polyethersulfone (PESH) membrane of 30 kDa. NaCl solutions at different salt concentrations, temperatures and crossflow velocities were used to clean the UF membranes tested. The cleaning efficiency was related to the MWCO, membrane material and operating conditions during fouling and cleaning steps. NaCl solutions were able to completely clean the membranes fouled with the WPC solutions at the lowest concentration tested. As WPC concentration increased, the hydraulic cleaning efficiency

(HCE) decreased. The results demonstrated that an increase in temperature and crossflow velocity of the cleaning solution caused an increase in the HCE. Regarding NaCl concentration, the HCE increased up to an optimal value. As the concentration was greater than this value, the cleaning efficiency decreased. In addition, an equation that correlates the cleaning efficiency to the operating parameters studied in this work (temperature, NaCl concentration, crossflow velocity in the cleaning procedure and WPC concentration during the fouling step) was developed and then, an optimization analysis was performed to determine the values of the parameters that lead to a 100 % cleaning efficiency.

Keywords: Ultrafiltration; membrane cleaning; whey protein concentrate; NaCl solutions

1. Introduction

Nowadays, whey is one of the most important by-products in dairy industries during cheese and casein production: 8-9 kg of whey are produced per each 1-2 kg of cheese [1]. Whey is rich in proteins, lactose, minerals and water-soluble vitamins. Thus, it is considered a valuable product for applications in food and pharmaceutical industries rather than a wastewater [2]. Among whey components, proteins have a high nutritional and functional value due to their high content of essential amino acids and their gelatinization and emulsifying properties [3].

Because of the interest of its protein fraction, whey is usually transformed to obtain whey protein concentrates (WPC) with a protein content of 35-80 % w/w in dry basis (31.23 – 234.3 $g\cdot L^{-1}$) and whey protein isolates (WPI) with more than 85 % w/w in dry basis (237.1 $g\cdot L^{-1}$) of protein content [2]. The manufacture of these products involves different processes: ultrafiltration (UF), diafiltration, concentration by evaporation under reduced pressure and spray drying [4]. However, during the UF process, the production efficiency is limited because of membrane fouling, which results in a decline in permeate flux. As proteins and minerals are the main foulants in whey and WPC solutions, several pretreatments can be performed in order to increase protein solubility and limit calcium phosphate precipitation and calcium bridging during the UF process [5].

As pretreatments are not enough to avoid membrane fouling, membranes have to be cleaned with conventional and non conventional techniques. In dairy industries, conventional cleaning agents as alkalis, acids and disinfectants are used in several washing steps [6-9]. However, in some cases, membrane lifetime may be reduced and a negative impact on the environment may be caused when these aggressive agents are used. To overcome these problems, some non conventional cleaning techniques have been developed in the last years [10-12]. For instance, the use of enzymes as cleaning agents has been reported by other authors as an effective alternative cleaning technique on membranes used for whey treatment [12, 13]. The main advantage of this technique is the utilization of mild pH values, so that the membranes may not be affected by acids and/or alkalis. Another innovative cleaning protocol is based on the utilization of saline solutions. Some authors [14-16] have reported the effect of cations and anions on the interactions among proteins. According to their capability to increase or decrease protein solubility, Hofmeister [14] proposed a ranking of salts. Based on the Hofmeister series, Tsumoto *et al.* [15] reported that some salts (such as NaCl) caused an increase in protein solubility (salting-in effect) while other salts (such as Na_2SO_4) decreased it (salting-out effect). Nucci and Vanderkooi [16] studied the ability of divalent and monovalent cations to precipitate proteins. They demonstrated that calcium is one of the most salting-out cations. This is in a good agreement with other works about the influence of calcium on protein bridging and membrane fouling [8, 17].

However, only a few papers are focused on the utilization of salts as membrane cleaning agents. Lee and Elimelech [18] tested NaCl solutions at different concentrations to clean reverse osmosis membranes fouled with alginate and calcium solutions. They achieved values of cleaning efficiency of about 90 % when a salt concentration of 50 mM was used. In a previous work, Corbatón-Báguena *et al.* [19] studied the influence of several salts (Na_2SO_4, NaCl, $NaNO_3$, NH_4Cl and KCl) on the cleaning efficiency of a 15 kDa ceramic UF membrane fouled with protein solutions. They demonstrated that chloride and nitrate salts were the most effective.

The aim of this work was to investigate the effectiveness of NaCl solutions to clean three different UF membranes fouled with WPC solutions at different concentrations. The effect of membrane material and MWCO on the effectiveness of the cleaning protocol was studied by testing a 15 kDa monotubular ceramic membrane, a 5 kDa flat-sheet polyethersulfone (PES) membrane and a 30 kDa flat-sheet permanently hydrophilic polyethersulfone (PESH) membrane. The influence of the operating conditions during the cleaning procedure (temperature, NaCl concentration and crossflow velocity) was also investigated. The best experimental cleaning conditions to achieve the highest cleaning efficiency were estimated by a statistical analysis.

2. Materials and methods

2.1. Materials

Renylat WPC solutions (Industrias Lácteas Asturianas S.A., Spain) at different concentrations (22.2, 33.3 and 150 $g \cdot L^{-1}$) were used as feed solutions during the fouling steps. WPC was supplied in powder form and it was dissolved in deionized water until the final concentration was achieved. Table 1 shows the composition of the WPC. Determination of each component in the WPC was performed as follows: total protein concentration was determined by means of the Bradford method (Sigma Aldrich, Germany) [20], lactose amount was estimated by reaction with 3,5-dinitrosalicylic acid (DNS, Sigma Aldrich, Germany) [21], ash content was calculated by using a muffle furnace at 540 ºC (AOAC method 930.30) [22], cations concentration was determined using a "790 Personal IC" chromatograph with a Metrosep C 2 150 column (both from Metrohm, Switzerland), anions concentration was obtained by using Spectroquant chloride and phosphate testing kits (Merck Millipore, Spain) [23] and fat content was measured by a MilkoScan FT120 (Gerber Instruments, Switzerland) [24]. Absorbance at 595 nm was measured by means of an UV-visible spectrophotometer (Hewlett-Packard 8453).

If initial membrane permeability was not completely recovered after the salt cleaning procedure, NaClO aqueous solutions (10 % w/v, Panreac, Spain) at pH 11 and 45 ºC and NaOH aqueous solutions (98 % purity, Panreac, Spain) at pH 11 and 45 ºC were used to clean the ceramic and polymeric membranes, respectively. These conventional cleaning protocols are in accordance with those suggested by the manufacturers.

2.2. Membranes

Three different UF membranes were used to perform the experiments: a monotubular ZrO_2-TiO_2 membrane of 15 kDa (TAMI Industries, France), a flat-sheet PES membrane of 5 kDa (UP005, Microdyn Nadir, Germany) and a flat-sheet PESH membrane of 30 kDa (UH030, Microdyn Nadir, Germany). The effective area of these membranes was 35.5 cm^2 for the ceramic membrane and 100 cm^2 for the polymeric membranes. These materials and MWCOs were selected in order to study their influence on the membrane cleaning efficiency. In addition, the MWCOs selected in this work are in the range of the typical MWCOs used in the manufacture and treatment of whey and WPC [25, 26].

2.3. Experimental set-up

Fouling and cleaning experiments were carried out in a VF-S11 UF plant (Orelis, France) with a stainless steel feed tank of 10 L. Crossflow velocity and pressure drop across the module were controlled by a variable speed volumetric pump and two manometers placed at the inlet and outlet sides of the module. Permeate flux was measured gravimetrically using a scale (0.001 g accuracy). All the experiments were performed in total recirculation mode, except the rinsing steps. The experimental set-up was described elsewhere [19].

2.4. Experimental procedure

2.4.1. Fouling experiments

Fouling experiments were performed in total recirculation mode at a transmembrane pressure of 2 bar, a crossflow velocity of 2 $m \cdot s^{-1}$ and a temperature of 25 ºC. In addition, different WPC concentrations were used to simulate the effect of the increase in protein concentration during the UF process. These operating conditions were selected according to the literature about whey protein UF [19, 27]. Permeate flux and rejection values were measured during the fouling step to ensure the reproducibility of all the runs with each feed solution. Each fouling test was repeated a minimum of 10 times.

Protein rejection was determined by Eq. 1 for all the membranes tested.

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

Where C_b is protein concentration in the WPC feed solution and C_p is protein concentration in the permeate.

2.4.2. Rinsing and cleaning experiments

Reversible fouling was removed from the membrane surface by rinsing the membranes with deionized water after the fouling step at a transmembrane pressure of 1 bar, different crossflow velocities (1.2-4.2 $m\cdot s^{-1}$) and 25 ºC with the permeate valve opened. Then, NaCl cleaning step was carried out to allow the removal of the irreversible fouling. Operating conditions during the cleaning step were the following: four different NaCl concentrations (0-7.5 mM), four temperatures (50-80 ºC) and the same transmembrane pressure and crossflow velocity as those considered for the rinsing step. The pH values of all the saline solutions ranged from 6.8 to 7. After the saline cleaning procedure, another washing step with deionized water was performed to completely remove the loose foulant molecules as well as the cleaning agent molecules from the membrane surface.

When permeate flux achieved the steady-state value, cleaning and rinsing steps ended. Duration of these steps was 45 min for the rinsing steps and 70-80 min for the cleaning step.

After the last rinsing step, a conventional chemical cleaning with alkaline solutions was performed if the initial permeability conditions were not achieved, as it was mentioned and described in the "Materials" section.

2.5. Evaluation of membrane cleanliness

The hydraulic efficiencies of the first rinsing step (HRE) and of the complete cleaning procedure (HCE), i.e. after the second rinsing step, were calculated using Eq. 2 and 3. Other authors [27, 28] reported equations to determine the efficiency of rinsing and cleaning steps when alkaline solutions were used to restore the initial permeability of the membranes. Their equations were based on a relation among the membrane hydraulic resistance obtained after each step (fouling, first rinsing, cleaning and second rinsing) by means of the Darcy's law. In this work, similar equations (Eq. 2 and 3) were proposed to calculate the hydraulic rinsing and cleaning efficiencies (HRE and HCE, respectively).

$$\text{HRE}\,(\%) = \left(\frac{R_f - R_{r1}}{R_f - R_m}\right)\cdot 100 \qquad \text{Eq. 2}$$

$$\text{HCE}\,(\%) = \left(\frac{R_f - R_{r2}}{R_f - R_m}\right)\cdot 100 \qquad \text{Eq. 3}$$

Where R_f is the fouling resistance, R_{r1} is the hydraulic resistance after the first rinsing step, R_{r2} is the hydraulic resistance after the second rinsing step and R_m is the resistance of the new membrane, which were calculated by means of the Darcy's law [19].

When HCE values obtained at the end of the cleaning procedure were of 100 %, the saline cleaning can substitute the conventional alkaline/acid cleaning, as the membrane permselective properties were completely restored.

3. Results and discussion

In order to calculate HCE for each membrane tested, the values of R_m were necessary. These values were: $9.453 \cdot 10^{12}$, $5.001 \cdot 10^{12}$ and $3.794 \cdot 10^{12}$ m^{-1}, for the membranes of 5, 15 and 30 kDa, respectively.

3.1. Fouling experiments

Fig. 1 shows the evolution of permeate flux with time for each membrane and feed solution tested. As it was expected, the higher the WPC concentration in the feed solution was, the lower the steady-state permeate flux was. This is due to the fact that an increase in protein concentration results in a more severe membrane fouling due to an increase in concentration polarization and adsorption phenomena as protein concentration increases. Regarding the permeate flux decline, the PESH 30 kDa membrane showed the lowest one for all the feed solutions tested compared with the other membranes. For instance, for the most severe fouling conditions (WPC concentration of 150 $g \cdot L^{-1}$), the percentage of permeate flux decline was 44.73, 56.64 and 26.84 % for the 5, 15 and 30 kDa membranes, respectively. The reason for that is the combination of low membrane surface roughness and high hydrophilicity of the PESH membrane in comparison with the PES and the ceramic membrane [29].

According to other authors [30-32], both high hydrophilicity and low surface roughness result in membranes with better antifouling properties. Evans *et al.* [31] studied the influence of surface roughness and membrane hydrophobicity on the UF of black tea using membranes made of different materials. They found that fouling was more severe in the case of the rougher and more hydrophobic membranes. Rahimpour and Madaeni [30] investigated the effect of the modification of the membrane with different hydrophilic monomers on the performance of several PES membranes during the filtration of non-skim milk. They demonstrated that, among all the modified and unmodified membranes tested, the highest protein rejection and lowest fouling resistances were obtained with the membranes that showed the most hydrophilic and smooth surfaces. García-Ivars *et al.* [32] also tested modified and unmodified PES membranes with different hydrophilicity and surface roughness in several fouling/rinsing cycles. They obtained better performances for the more hydrophilic and less rougher membranes. All these results are in good agreement with the results obtained in this work. According to the AFM measurements for the new membranes described by the authors elsewhere [19], the values of Root Mean Square roughness (R_q) were 0.487, 17.900 and 1.657 nm for the 5, 15 and 30 kDa membranes, respectively. On the other hand, while the 5 kDa membrane was hydrophobic, the 15 and 30 kDa membranes were hydrophilic. Therefore, the lowest permeate flux decline was obtained for the 30 kDa membrane, followed by the 5 and 15 kDa membranes for all the feed solutions tested.

Fig. 2 shows the changes on protein rejection values with time for all the membranes and feed solutions considered. As WPC concentration increased, the steady-state rejection values slightly decreased for all the membranes tested. Mathew *et al.* [33] also studied the influence of protein concentration on the percentage of rejection. They demonstrated that an increase in protein concentration resulted in a decrease in the rejection values using multilayer membranes with the same number of bilayers.

3.2. Cleaning experiments

3.2.1. Effect of NaCl concentration on HCE

The influence of NaCl concentration on the effectiveness of the cleaning protocol is shown in Fig. 3. The rest of experimental conditions were set at 50 ºC and 2.18 $m\cdot s^{-1}$ (for the 5 and 30 kDa membranes) and 4.2 $m\cdot s^{-1}$ (for the 15 kDa membrane). These different crossflow velocities were selected due to the higher surface roughness of the ceramic membrane in comparison with the polymeric ones. The rougher the membrane surface was, the more severe the fouling was and thus, the highest crossflow velocity that can be achieved in the experimental set-up was selected in order to remove the foulant deposits.

As it can be observed in Fig. 3, an increase in salt concentration resulted in an increase in the values of HCE for each membrane tested when a WPC concentration of 22.2 $g\cdot L^{-1}$ was used. NaCl concentration ranged from 0 (deionized water) to 7.5 mM, according to previous studies about salt cleaning of protein fouled membranes [34], and the highest values of HCE were obtained at a NaCl concentration of 5 mM in all the cases. The efficiency of NaCl to clean membranes fouled with protein solutions was also reported in the literature. Lee and Elimelech [18] investigated the effect of NaCl concentration on the cleaning efficiency of reverse osmosis membranes that were fouled with feed solutions containing alginate and calcium. They reported that values of cleaning efficiency of 90 % were achieved at NaCl concentrations of 50 mM due to a decrease in foulant-foulant adhesion forces caused by the salt solutions, while using higher salt concentrations (100-300 mM) did not result in higher efficiency values.

It can also be observed in Fig. 3 that a greater increase in the concentration of NaCl above 5 mM caused a decrease in HCE. This may be due to the fact that fouling and cleaning mechanisms became competitive and the experimental conditions used did not favour the effective mass transfer of foulant molecules from the membrane surface back to the bulk solution [35]. In addition, other authors demonstrated the effect of salt solutions and their concentration on protein solubility. Hofmeister [14] ranked different cations and anions depending of their ability to act as protein stabilizers. As a consequence, ions were divided into salting-in or salting-out depending on the increase or decrease in protein solubility that they caused, respectively. Based on the Hofmeister series, Tsumoto *et al.* [15] observed that low surface tension favours the salting-in effects of salt solutions. Since surface tension decreases when salt concentration increases at low salt concentrations, the effectiveness of NaCl as a cleaning agent is enhanced at low NaCl concentrations. On the other hand, Zhang [36] demonstrated that Cl^- can specifically bind to the protein surface and proposed a mechanism to explain why this phenomenon takes place. The law of matching water affinities states that ions with similar water affinity tend to bond each others. According to this law, Cl^- is a weakly hydrated monovalent anion and thus, it preferably binds to the positive-charged side chains of the proteins as well as the non-polar groups. As a result, Cl^- may act as a binding agent to the protein surface and facilitates their removal from the membrane surface.

In addition, the highest HCE values were achieved with the 30 kDa membrane for all the NaCl concentrations tested. As it was above mentioned, high hydrophilicity and low surface roughness favour the membrane antifouling properties and thus, milder experimental conditions have to be used in order to clean such membrane. For this reason, at the same salt concentration, temperature and crossflow velocity, the 30 kDa membrane showed the highest values of HCE.

3.2.2. Effect of temperature on HCE

In order to increase the HCE values obtained for the best NaCl concentration (see Fig. 3), several cleaning experiments at different temperatures were performed. In this way, temperatures ranging from 50 to 80 ºC were tested to study the influence of this parameter on HCE, while the other experimental conditions were maintained constant for all the experiments at a NaCl concentration of 5 mM and crossflow velocities of 2.18 $m \cdot s^{-1}$ (for the 5 and 30 kDa membranes) and 4.2 $m \cdot s^{-1}$ (for the 15 kDa membrane).

Fig. 4 shows the values of HCE for the different temperatures and membranes tested. Increasing the temperature of the cleaning solution from 50 to 80 ºC resulted in an increase in HCE, achieving efficiency values of 100 % at the highest temperature for all the membranes used when the fouling experiments were performed with a WPC concentration of 22.2 $g \cdot L^{-1}$. As it was above mentioned, the lower the surface tension is, the greater the salting-in effect is [15]. High temperatures lead to a decrease in the surface tension, which enhances the effectiveness of NaCl as cleaning agent. The interactions salt-proteins also increased as the temperature of the cleaning solution increased, due to the effect of temperature on the diffusivity coefficient. In this way, an increase in temperature causes an increase in that coefficient, which results in an enhancement of the mass transfer process of protein molecules from the membrane surface to the bulk solution [18].

3.2.3. Effect of crossflow velocity on HCE

Membranes fouled with WPC solutions of 22.2 $g \cdot L^{-1}$ were cleaned at a NaCl concentration of 5 mM, a temperature of 80 ºC and different crossflow velocities to study the influence of this operating parameter on the HCE values. As it is shown in Fig. 5, an increase in crossflow velocity from 1.2 to 2.18 $m \cdot s^{-1}$ caused an increase in the HCE values obtained for all the membranes tested. The greatest HCE (about 100 %) was achieved at a crossflow velocity of 2.18 $m \cdot s^{-1}$.

As Lee *et al.* [37] demonstrated, the higher the crossflow velocity during the cleaning procedure of a PES UF membrane was, the higher the flux recovery was. These authors achieved approximately the same permeate flux as that at the beginning of the UF process, removing the gel layer formed by natural organic matter on the membrane surface. This is in accordance with the fact that a crossflow velocity value about 2.18 $m \cdot s^{-1}$ was the optimal to effectively clean the membranes tested in this work.

3.2.4. Effect of WPC concentration on HCE

Fig. 6 shows the effect of WPC concentration during the fouling step on the HCE values obtained at the end of the cleaning procedure. Firstly, membranes fouled with WPC solutions at 22.2 and 33.3 $g \cdot L^{-1}$ were cleaned with NaCl solutions at the best cleaning conditions above mentioned (NaCl concentration of 5 mM, temperature of 80 ºC and a crossflow velocity of 2.18 $m \cdot s^{-1}$). As it can be observed in Fig. 6, the HRE and HCE values decreased for all the membranes tested as the WPC concentration in the feed solution increased, due to the more severe fouling caused on the membranes. In a previous work, Corbatón-Báguena *et al.* [29] investigated the fouling mechanisms dominating the UF of WPC solutions on ceramic and polymeric membranes by fitting several mathematical models. They confirmed that both complete blocking and cake formation were the main fouling mechanisms responsible for membrane fouling and that an increase in WPC concentration in the feed solution during the fouling step caused a more severe fouling on the membrane surface because the values of the model parameters increased as the WPC concentration increased. They observed that the resistance due to concentration polarization and adsorption as well as the resistance due to cake formation increased for all the membranes tested when WPC concentration increased from 22.2 to 33.3 $g \cdot L^{-1}$.

In order to obtain higher HCE results, the crossflow velocity during the cleaning step was increased at 4.2 $m \cdot s^{-1}$. At this new value, two different WPC concentrations were tested (33.3 and 150.0 $g \cdot L^{-1}$). Comparing the HRE and HCE values achieved at 2.18 and 4.2 $m \cdot s^{-1}$ when a WPC concentration of 33.3 $g \cdot L^{-1}$ was used in the fouling step, it can be observed that, although slightly higher HRE was obtained when crossflow velocity increased, almost identical HCE results were obtained for all the membranes tested. This indicated that this increase in crossflow velocity could not completely remove the protein deposits on the membrane surface and thus, did not result in an increase in the HCE values. This pattern also occurred when the WPC concentration increased up to 150.0 g·L^{-1}. In this case, the HCE achieved was the same as that obtained for all the membranes fouled with a WPC concentration of 33.3 g·L^{-1}. Therefore, there is a maximum quantity of proteins that can be removed from the membrane surface when NaCl solutions were used as cleaning agents and as a consequence, a maximum HCE of about 90-95 % can be achieved with this cleaning method at the highest WPC concentration tested.

3.2.5. Statistical and optimization analysis

An equation that relates HCE to the operating conditions and their interactions was developed by means of the Statgraphics software (Eq. 4). These conditions were: temperature during cleaning step, T; NaCl concentration, C_{NaCl}; crossflow velocity, v; membrane surface roughness, R_q and WPC concentration during the fouling step, C_{WPC}. The regression coefficient R^2 for Eq. 4 was 0.980 at a confidence level of 95 % (p-values lower than 0.05).

$$\begin{aligned}\text{HCE (\%)} = {} & 303.028 - 3.392 \cdot T + 10.236 \cdot C_{NaCl} - 123.544 \cdot v + 17.930 \cdot R_q - 0.719 \cdot {C_{NaCl}}^2 - 2.197 \cdot v^2 - \\ & - 0.183 \cdot {R_q}^2 + 0.006 \cdot {C_{WPC}}^2 + 1.864 \cdot T \cdot v - 0.181 \cdot T \cdot R_q - 0.636 \cdot C_{NaCl} \cdot v - 0.267 \cdot v \cdot C_{WPC}\end{aligned} \qquad \text{Eq. 4}$$

To obtain the optimal conditions resulting in a HCE value of 100 %, the Microsoft Excel Solver tool was used. Those optimal conditions were a temperature of 80.00 ºC, a NaCl concentration of 5.01 mM, a crossflow velocity of 2.23 m·s^{-1}, a membrane surface roughness of 2.02 nm and a WPC concentration of 22.19 g·L^{-1}. These values are in a good agreement with those related to the best conditions to obtain the highest HCE observed in Figs. 2-5 for the PESH 30 kDa membrane used (R_q = 1.657). Therefore, low membrane roughness favours the cleaning process at milder conditions of crossflow velocity and cleaning agent concentration, while high temperatures result in greater cleaning efficiency values when low protein concentration in the fouling feed solution was used.

4. Conclusions

NaCl solutions were able to effectively clean three UF membranes of different materials and MWCOs (a PES membrane of 5 kDa, a ceramic ZrO_2-TiO_2 membrane of 15 kDa and a PESH membrane of 30 kDa) fouled with WPC solutions, resulting in high values of HCE for all the membranes and WPC solutions tested.

Cleaning results demonstrated that an increase in temperature and crossflow velocity of the cleaning solution caused an increase in the HCE. Regarding NaCl concentration, there was an optimal value up to which the HCE increased (about 5 mM for all the membranes tested). When the concentration was greater than this value, the cleaning efficiency decreased possibly due to the competition between cleaning and fouling mechanisms and the reduction in surface tension. On the other hand, the higher the WPC concentration in the feed solution during the fouling step was, the lower the HCE was, due to the more severe fouling caused when protein concentration in the feed solution increased. The highest values of the cleaning efficiency (100 %) were achieved for the lowest WPC concentration tested (22.2 $g \cdot L^{-1}$).

An equation that correlates the HCE to the operating parameters (temperature, NaCl concentration, crossflow velocity in the cleaning procedure and WPC concentration during the fouling step) was obtained with high accuracy ($R^2 = 0.980$) at a confidence level of 95

%. The optimization analysis performed showed that a temperature of 80.00 ºC, a NaCl concentration of 5.01 mM, a crossflow velocity of 2.23 m·s^{-1}, a membrane surface roughness of 2.02 nm and a WPC concentration of 22.19 g·L^{-1} resulted in a 100 % of HCE, which corresponded to the best conditions experimentally obtained for the 30 kDa membrane.

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Nomenclature

List of symbols

C_b	Protein concentration in the feed solution (g·L^{-1})
C_{NaCl}	NaCl concentration (mM)
C_p	Protein concentration in the permeate (g·L^{-1})
C_{WPC}	WPC concentration in the feed solutions (g·L^{-1})
J	Permeate flux (m^3·m^{-2}·s^{-1})
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_{r2}	Resistance after the second rinsing step (m^{-1})
R_q	Root Mean Square Roughness (nm)
t	Filtration time (s)
T	Temperature of the cleaning solution (ºC)
v	Crossflow velocity ($m \cdot s^{-1}$)

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
UF	Ultrafiltration
WPC	Whey protein concentrate

References

[1] C. Baldasso, T.C. Barros, I.C. Tessaro, Concentration and purification of whey proteins by ultrafiltration, Desalination 278 (2011) 381-386.

[2] B. Sanmartín, O. Díaz, L. Rodríguez-Turienzo, A. Cobos, Composition of caprime whey protein concentrates produced by membrane technology after clarification of cheese whey, Small Rum. Res. 105 (2012) 186-192.

[3] J.N. Wit, Nutritional and functional characteristics of whey proteins in food products, J. Dairy Sci. 81 (1998) 597-608.

[4] R. Hussain, C. Gaiani, J. Scher, From high milk protein powders to the rehydrated dispersions in variable ionic environments: A review, J. Food Eng. 113 (2012) 486-503.

[5] M.C. Adams, J. Zulewska, D.M. Barbano, Effect of annatto addition and bleaching treatments on ultrafiltration flux during production of 80 % whey protein concentrate and 80 % serum protein concentrate, J. Dairy Sci. 96 (2013) 2035-2047.

[6] 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.

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

[8] 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.

[9] 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.

[10] 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.

[11] 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.

[12] M.A. Argüello, S. Álvarez, F.A. Riera, R. Álvarez, Enzymatic cleaning of inorganic ultrafiltration membranes used for whey protein fractionation, J. Membr. Sci. 216 (2003) 121-134.

[13] M.A. Argüello, S. Álvarez, F.A. Riera, R. Álvarez, Utilization of enzymatic detergents to clean inorganic membranes fouled by whey proteins, Sep. Purif. Technol. 41 (2005) 147-154.

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

[15] 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.

[16] 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.

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

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

[19] 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.

[20] M.M. Bradford, A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein-dye binding, Analytical Biochem 72 (1976) 248-254.

[21] G.L. Miller, Use of dinitrosalicylic acid reagent for determination of reducing sugar, Anal. Chem. 31 (1959) 426-428.

[22] AOAC Official Method 930.30, 1930, Ash of Cried Milk, first action 1930.

[23] W.C. Mak, C. Chan, J. Barford, R. Rennerberg, Biosensor for rapid phosphate monitoring in a sequencing batch reactor (SBR) system, Biosensors and bioelectronics 19 (2003) 233-237.

[24] S. Chessa, O. Bulgari, R. Rizzi, L. Calamari, P. Bani, S. Biffani, A.M. Caroli, Selection for milk coagulation properties predicted by Fourier transform infrared spectroscopy in the Italian Holstein-Friesian breed, J. Dairy Sci. 97 (2014) 4512-4521.

[25] P.G. Hobman, Ultrafiltration and manufacture of whey protein concentrates in J.G. Zadow (Ed.) Whey and Lactose Processing, Elsevier Science Publishing CO., INC., 1992, pp. 195-230.

[26] C. Marella, K. Muthukumarappan, L.E. Metzger, Evaluation of commercially available, wide-pore ultrafiltration membranes for production of α-lactalbumin-enriched whey protein concentrate, J. Dairy Sci. 94 (2011) 1165-1175.

[27] 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.

[28] 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.

[29] M.-J. Corbatón.Báguena, S. Álvarez-Blanco, M.-C. Vincent-Vela, Fouling mechanisms of ultrafiltration membranes fouled with whey model solutions, Desalination 360 (2015) 87-96.

[30] 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.

[31] 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.

[32] J. García-Ivars, M-I. Iborra-Clar, M-I. Alcaina-Miranda, J-A. Mendoza-Roca, L. Pastor-Alcañiz, Development of fouling-resistant polyethersulfone ultrafiltration membranes via surface UV photografting with polyethylene glycol/aluminum oxide nanoparticles, Sep. Purif. Technol. 135 (2014) 88-99.

[33] J. Mathew, C.T. Aravindakumar, U.K. Aravind, Effect of ionic strength and protein concentration on the transport of proteins through chitosan/polystyrene sulfonate multilayer membrane, J. Membr. Sci. 325 (2008) 625-632.

[34] M-J. Corbatón-Báguena, S. Álvarez-Blanco, M-C. Vincent-Vela, Salt cleaning of ultrafiltration membranes fouled by whey model solutions, Sep. Purif. Technol. 132 (2014) 226-233.

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

[36] 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.

[37] H. Lee, G. Amy, J. Cho, Y. Yoon, S.-H. Moon, I.S. Kim, Cleaning strategies for flux recovery of an ultrafiltration membrane fouled by natural organic matter, Wat. Res. 35 (2001) 3301-3308.

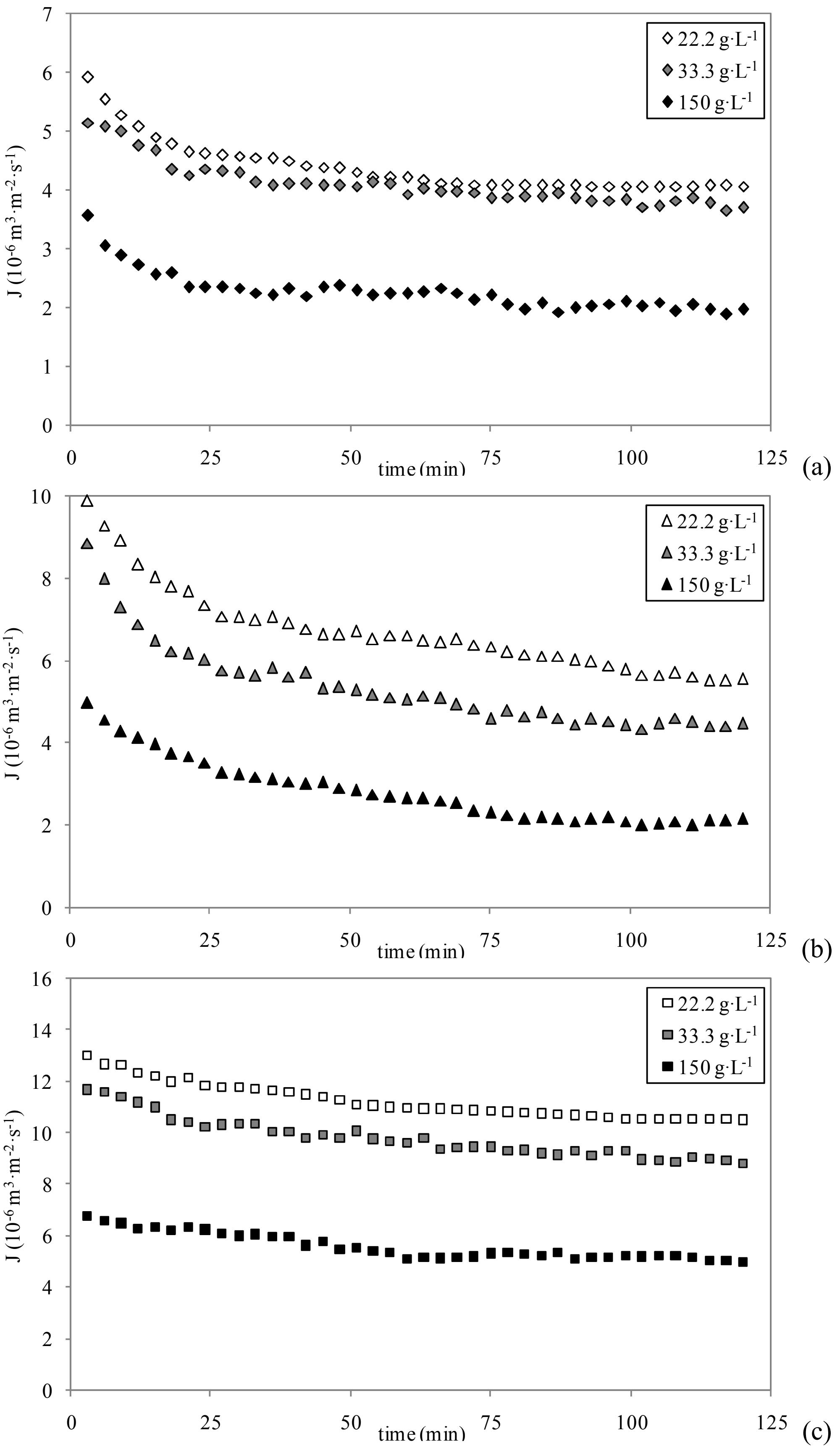

Fig.1. Evolution of permeate flux with time for the 5 kDa (a), 15 kDa (b) and 30 kDa (c) membranes with WPC solutions at different concentrations.

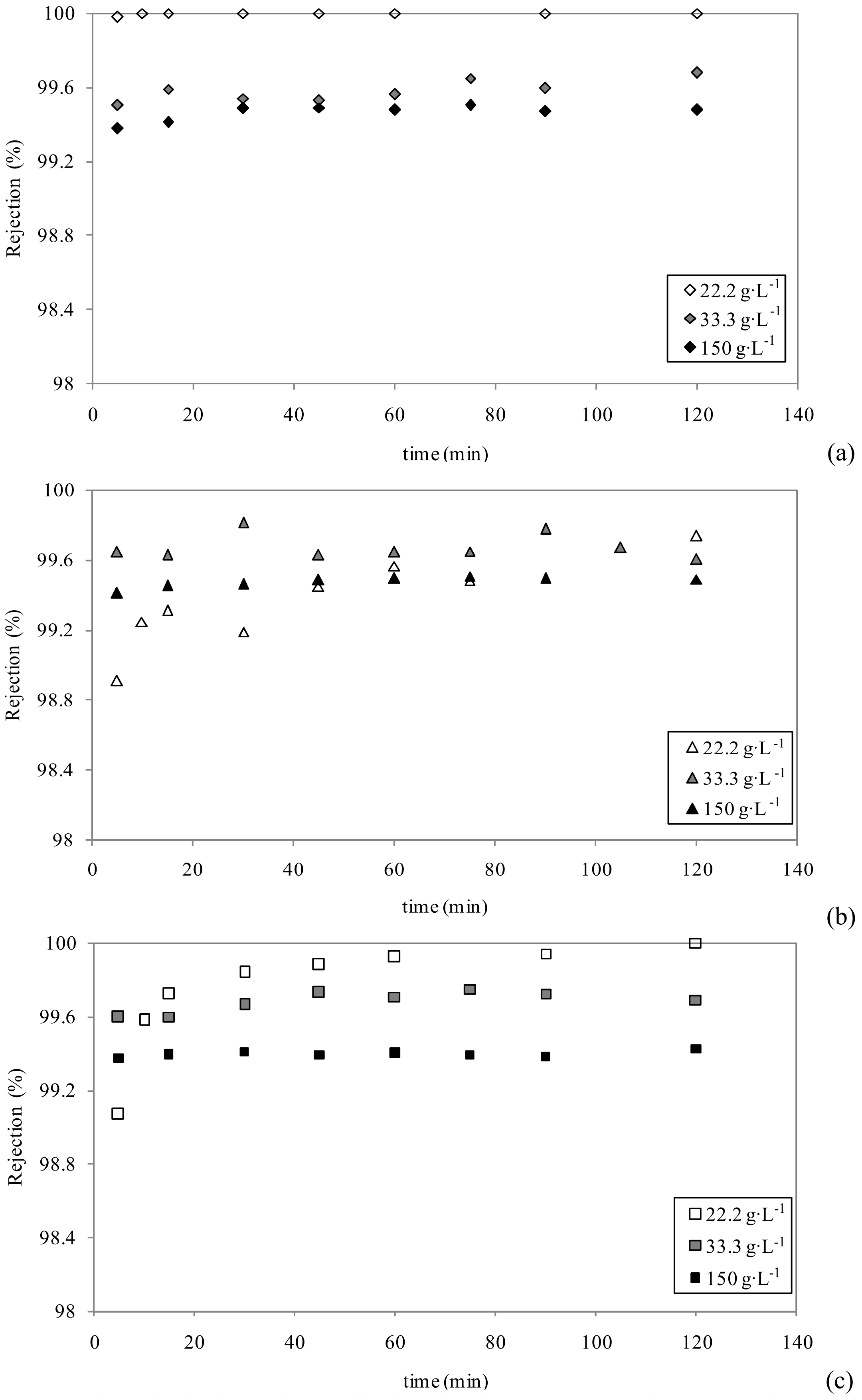

Fig.2. Evolution of rejection values with time for the 5 kDa (a), 15 kDa (b) and 30 kDa (c) membranes with WPC solutions at different concentrations.

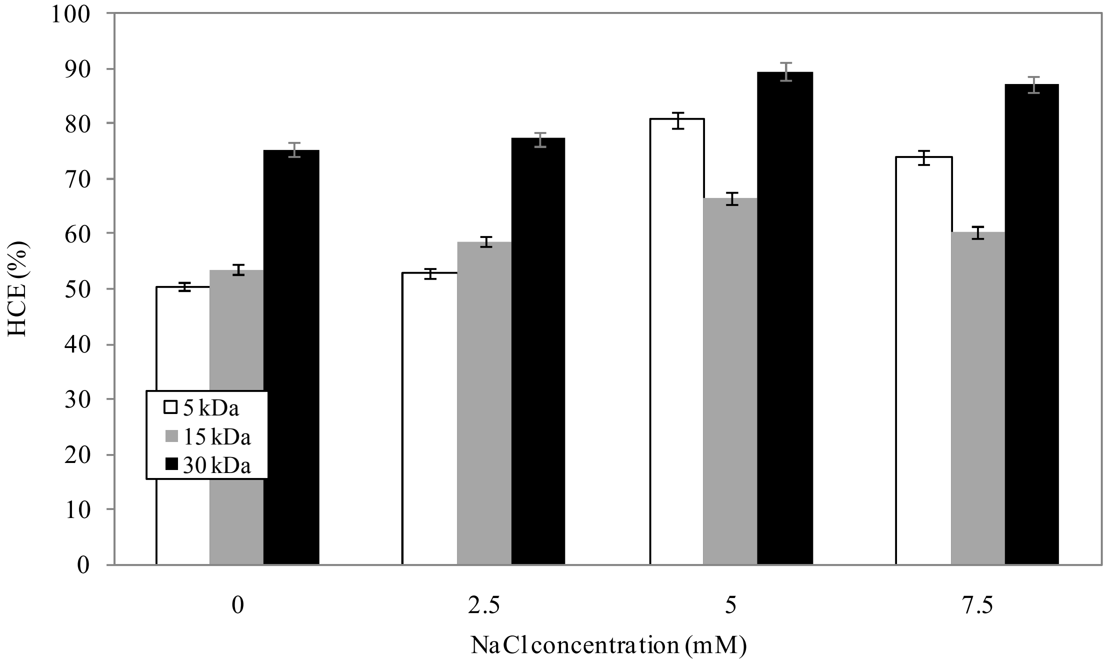

Fig. 3. Effect of NaCl concentration on HCE (WPC concentration: 22.2 g·L^{-1}; temperature: 50 ºC; crossflow velocity: 2.18 m·s^{-1} for the 5 and 30 kDa membranes and 4.2 m·s^{-1} for the 15 kDa membrane).

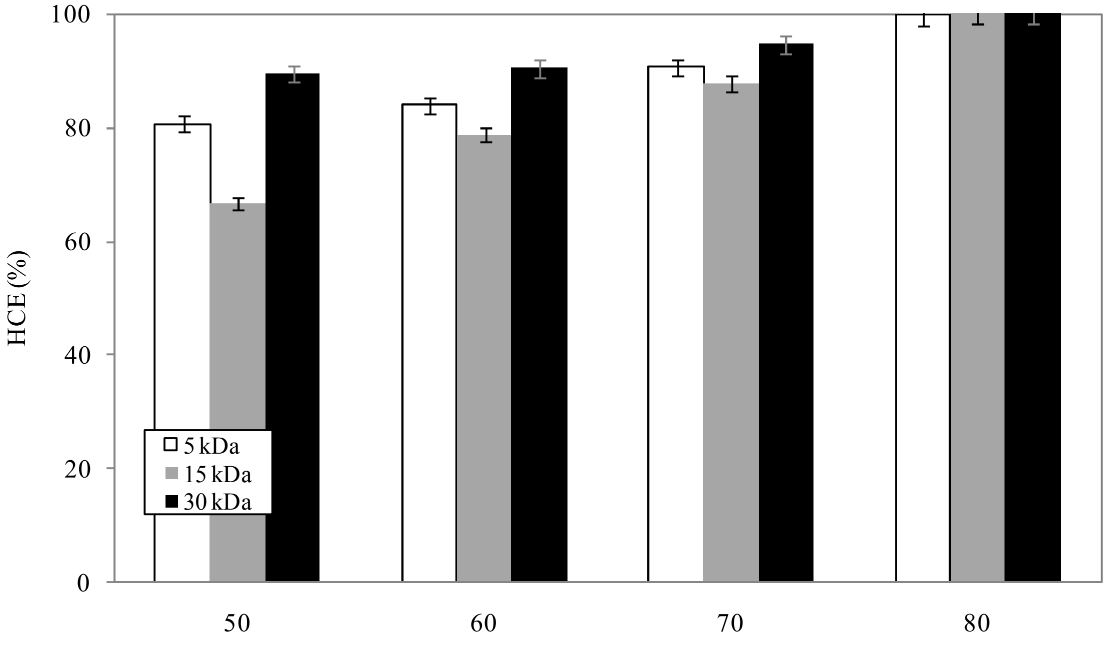

Fig. 4. Effect of temperature on HCE (WPC concentration: 22.2 g·L^{-1}; NaCl concentration: 5 mM; crossflow velocity: 2.18 m·s^{-1} for the 5 and 30 kDa membranes and 4.2 m·s^{-1} for the 15 kDa membrane).

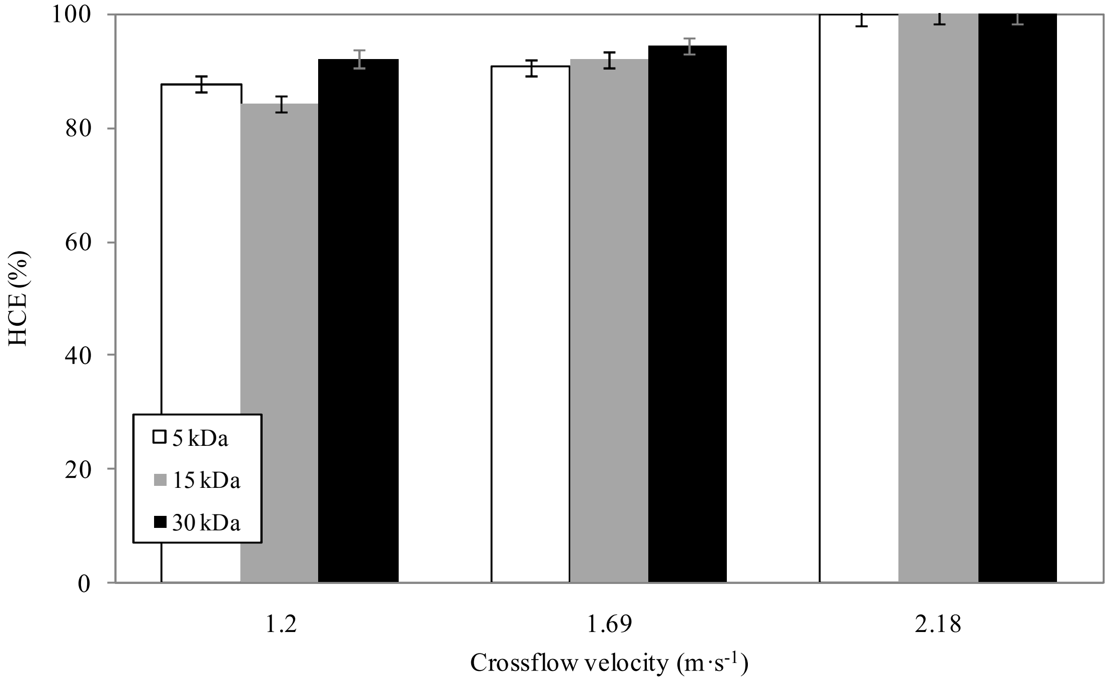

Fig. 5. Effect of crossflow velocity on HCE (WPC concentration: 22.2 g·L^{-1}; NaCl concentration: 5 mM; temperature: 80 ºC).

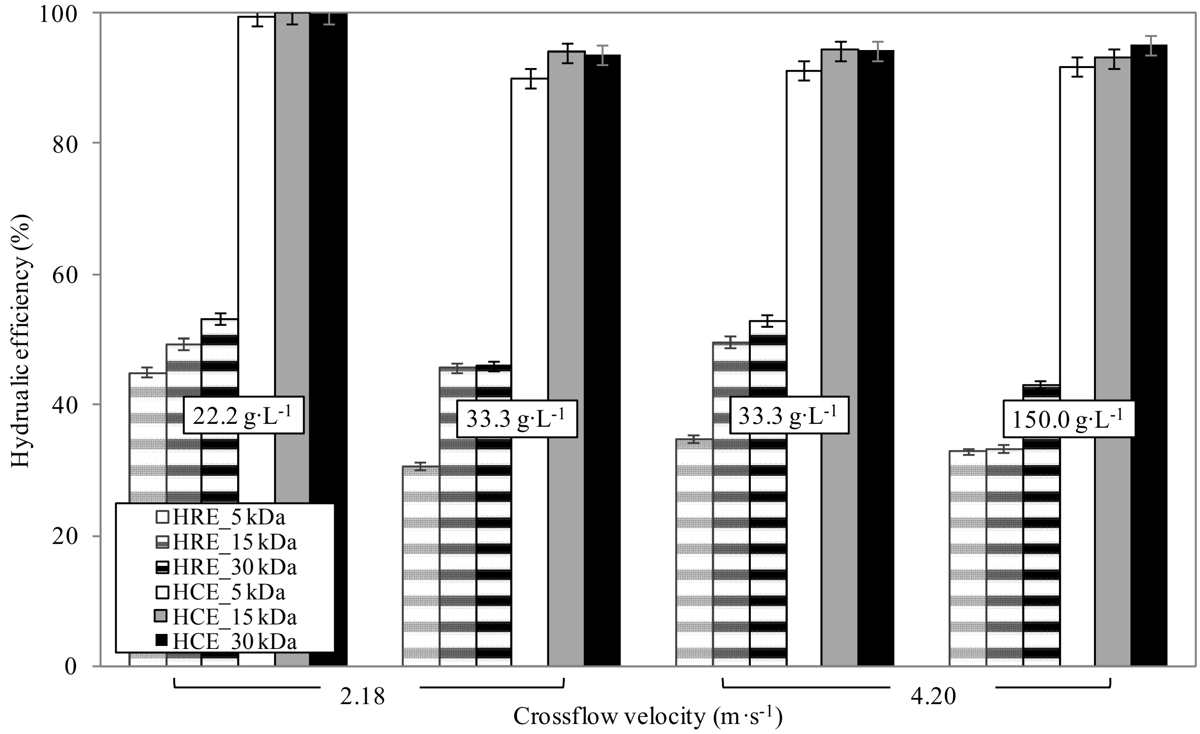

Fig. 6. Effect of WPC concentration during fouling step on HRE and HCE at different crossflow velocities (NaCl concentration: 5 mM; temperature: 80 ºC).

Table 1.
Composition of the commercial Renylat WPC used.

Component	Weight percentage in dry basis (% w/w)
Dry matter	93.66 ± 0.95
Proteins	40.74 ± 0.79
Lactose	38.27 ± 0.49
Fat	8.14 ± 0.20
Ash	7.85 ± 0.07
Ca	0.79 ± 0.06
Na	1.21 ± 0.09
K	1.42 ± 0.02
Cl	4.07 ± 0.24
PO_4-P	0.37 ± 0.03