Lujan Facundo, MJ.; Mendoza Roca, JA.; Cuartas Uribe, BE.; Alvarez Blanco, S. (2017). Membrane fouling in whey processing and subsequent cleaning with ultrasounds for a more sustainable process. Journal of Cleaner Production. 143:804-813. doi:10.1016/j.jclepro.2016.12.043

The manuscript has 5796 words including tables and figures.

Membrane fouling in whey processing and subsequent cleaning with ultrasounds for a more sustainable process.

María-José Luján-Facundo*, José-Antonio Mendoza-Roca, Beatriz Cuartas-Uribe, Silvia Álvarez-Blanco.

Instituto de Seguridad Industrial, Radiofísica y Medioambiental, Universitat Politècnica de València, Camino de Vera, s/n, Valencia 46022, Spain.

Tel. +34963876386
e-mail: malufa@etsii.upv.es

Keywords: Ultrasounds; ultrafiltration; model dairy solutions; fouling; membrane cleaning.

Abstract

Cost reduction and minimization of environmental impacts, based on by-product recovery, is the objective of applying the ultrafiltration technology for the treatment of cheese whey. In this work, ultrafiltration process was studied in an integrated way (filtration and membrane cleaning), focusing especially on the membrane cleaning. Membrane cleaning experiments were carried out with and without ultrasounds to evaluate the effect of ultrasounds on the membrane cleaning efficiency and, as a result, to reduce the consumption of chemicals. Tests were performed with two ultrafiltration polymeric membranes with molecular weight cut-offs of 30,000 Da (UH030) and 5,000 Da (UP005). Fouling experiments were carried out with Renylat whey protein concentrate solutions and $CaCl_2$ addition at a transmembrane pressure of 2 bar and cross flow velocity of 2 m/s during 2 h. Results showed that the presence of calcium increased the membrane fouling of both membranes. For UH030 membrane the reversible fouling prevailed over the irreversible fouling, meanwhile for UP005 membrane the irreversible fouling was the predominant one. Cleaning efficiency results demonstrated that ultrasounds application is an effective technique to clean ultrafiltration membranes after being fouled with whey protein concentrate solutions and may have a paramount importance on the overall process efficiency.

1. Introduction

Dairy industry is the main producer of liquid wastes in the food industry sector (Mirabella et al., 2014). The quantity of waste streams from cheese manufacturing industry has increased due to the rise in cheese production. 10 kg of milk are needed for the production of 1 kg of cheese and 9 kg of cheese whey are generated. Whey is a greenish-yellow liquid by-product of cheese production highly contaminated and with a high organic load around (100,000 mg O_2/L COD) (Carlini et al., 2015). About 85% of the total milk used in the cheese production is eliminated as whey (Parashar et al., 2016). In this context, worldwide, $40.7 \cdot 10^5$ tonnes of cheese whey per year are originated (Prazeres et al., 2012). Whey is rich in valuable components like proteins, lactose or minerals (calcium, magnesium or phosphorous) which makes that the valorization and reuse of this by-product acquires a paramount importance (Yorgun et al., 2008).

Pressure-driven membrane separation processes, such as reverse osmosis, nanofiltration (NF), ultrafiltration or microfiltration, can be used for the recovery of solid components from cheese whey. Regarding with NF technique, (Nguyen et al., 2003) studied the by-product recovery from cottage cheese whey production. Specifically, in dairy industry, ultrafiltration (UF) is commonly employed in the processing and whey treatment (Pal and Nayak, 2016). The pore size of the UF membranes is typically in the range of 1-100 nm. Therefore, they are suitable to retain molecules in the molecular weight range of 300-500,000 Da (like proteins), while the lactose and mineral salts would permeate through the membrane pores. Membrane technique represents an excellent alternative in the field of separation process due to cost reduction and to the improvement of the nutritional and functional proteins properties (Bhattacharjee et al., 2006). In this way, Cassini et al. (2010) tested UF membranes with pore size between 8-50 kDa to isolated soy protein from waste water.

However, the main problem in the performance of the UF process is the permeate flux reduction as a result of both concentration polarization (accumulation of solute at the membrane surface) and membrane fouling. In dairy industry, the main components involved in membrane fouling are proteins and ions, specifically calcium and phosphorous (Gsan et al., 1995). These molecules can cause membrane fouling, both by adsorption onto the membrane surface and pore blocking (Juang and Lin, 2004). In this way, membrane cleaning is an important stage of a membrane process that must be frequently carried out to remove fouling. Cleaning methods can be divided into chemical and physical. Although chemical methods are the most commonly used, they require large volumes of chemicals and can cause the degradation of the membrane material. In addition to it, the use of chemicals as sodium hypochlorite leads to generate effluents from the cleaning stage with organochlorine compounds. Because of that, it is

important taking into account physical methods, like ultrasounds that is a non-conventional physical cleaning method (Shi et al., 2014). Its use may reduce the use of chemicals leading to a cleaner process (Chi-Chuan et al., 2016).

In this way, Alventosa-deLara et al. (2014) studied the ultrasounds (US) application to clean ceramic UF membranes. These authors reported that the highest cleaning efficiencies were achieved at the lowest US frequencies. Wang et al., (2013) applied US-assisted chemical cleaning to clean UF membranes fouled with lactic acid fermentation broth. These researchers found that with the assistance of US, the membrane water flux was restored up to 97.5%. Similar results were obtained by (Maskooki et al., 2008), who studied US combined with alkaline solutions and they published that US have a synergistic effect with chemical agents to clean membranes.

In previous studies (Luján-Facundo et al., 2013, 2016), the application of US to chemical cleaning solutions of sodium hydroxide and surfactant after membrane fouling with different protein model solutions was studied. Results showed that US application was effective to clean UF membranes, both organic and inorganic membranes, especially when cleaning efficiency without US application was lower than 90%.

The main purpose of this study was to evaluate the UF process of dairy whey in an integrated way (filtration plus membrane cleaning). For it, firstly, membrane fouling was evaluated and modeled by the membrane resistances in-series and by the Hermia's models, and secondly, the membrane cleaning was evaluated. Thus, the use of US to reduce the consumption of chemicals and consequently to achieve a more sustainable process has been studied. Unlike other authors, US were applied in the cleaning solution tank instead of submerging the membrane module in the US bath. The influence of the calcium concentration in the membrane feed solution on the UF and on the cleaning step has also been studied. An economical study about the costs of the chemical cleaning step has been also performed. Summarizing, the main contribution of our work is focused on the proposal of an alternative and novel cleaning procedure for the membranes used in whey processing, which avoids the use of aggressive chemicals driving to environmental and economical benefits. Furthermore, all the process including modeling has been evaluated.

2. Materials and methods

2.1. Materials

Whey protein concentrate (WPC) type Renylat (Industrias Lácteas Asturianas S.A., Spain) at a concentration of 22.2 $g \cdot L^{-1}$ and different calcium concentrations (Table 1) were used as feed solution in the fouling step. WPC was received in a powder form and then it was dissolved in deionized water until the aimed concentration ($22 g \cdot L^{-1}$).

Renylat mainly consist of lactose (63.72% w/w) and proteins (38.14% w/w). The composition was described in a previous study (Luján-Facundo et al., 2016).

$CaCl_2$ (95% purity) was supplied by Panreac (Spain). Finally, as a cleaning agent an aqueous solution of NaOH (98% purity, Panreac, Spain) was tested at a pH of 11 and temperature of 25ºC.

Five fouling solutions were prepared for the experiments. Their composition is summarized in Table 1.

Table 1: Fouling solutions tested.

Fouling Solution	Solution composition	Concentration ($g \cdot L^{-1}$)
1	Renylat 45	22.22
	$CaCl_2$	0
2	Renylat 45	22.22
	$CaCl_2$	0.438
3	Renylat 45	22.22
	$CaCl_2$	0.876
4	Renylat 45	22.22
	$CaCl_2$	1.314
5	Renylat 45	22.22
	$CaCl_2$	1.752

2.2. Membranes

Two different UF membranes from Microdyn Nadir (Germany) were used to carry out the experiments: a flat-sheet polyethersulfone (PES) membrane with a molecular weight cut-off of 5,000 Da (membrane UP005) and a flat-sheet hydrophilic PES membrane with a molecular weight cut-off of 30,000 Da (membrane UH030). The effective area of these membranes was 100 cm^2 each one. According to the supplier data, the maximum temperature allowed by these membranes was 95ºC and the working pH is in the range 0-14. The membrane module employed was a Rayflow flat-sheet module, from Orelis (France) and with capacity for two flat-sheet membranes.

2.3. UF pilot plant

The UF pilot plant used for the experiments is from Orelis (France). The main elements are: a variable speed volumetric pump, a flowmeter and two manometers placed at both sides (inlet and outlet) of the membrane module. The US equipment consisted of a US generator and a US bath (both supplied by TSD Machinery, USA), which also worked as a feed tank. More details were given in a previous study (Luján-Facundo et al., 2013).

2.4. Experimental procedure

The following stages were carried out in every experiment: initial membrane permeability measurement, membrane fouling, membrane cleaning and a final membrane permeability measurement.

Permeability measurements were carried out with distilled water, at 25ºC and in the pressure range between 1-3 bars.

2.4.1. Fouling experiments

All the fouling tests were carried out in total recirculation mode, at a transmembrane pressure of 2 bar, at crossflow velocity of 2 $m \cdot s^{-1}$, for 2 h and at temperature of 25ºC. These experimental conditions were chosen taking into account previous works (Corbatón-Báguena et al., 2014) about whey protein UF processes. This group of authors carried out the cleaning step also at a pressure of 2 bar, at a crossflow velocity of 2 $m \cdot s^{-1}$, for 2 h and at a temperature of 25ºC. During the fouling stage flux was measured each 3 min using a precision balance KB-800-2 (Kern, Germany) with and accuracy of ± 0.01 g.

2.4.2. Cleaning experiments

Membrane cleaning experiments include three steps: first rinsing, chemical cleaning (where US were applied) and final rinsing.

The first rinsing was carried out to remove reversible fouling from the membrane surface and it was performed for 30 minutes with distilled water at a transmembrane pressure of 1 bar, cross flow velocity of 2.4 $m \cdot s^{-1}$ and a temperature of 25ºC . Then, the chemical cleaning was carried out with NaOH solution at pH 11 and 25ºC. Ultrasounds were applied to the chemical cleaning solution in half of the tests, at a frequency of 20 kHz and power of 300 W. These experimental conditions were chosen taking into account the results published by (Luján-Facundo et al., 2013). After the chemical

cleaning procedure, another rinsing step also with distilled water was performed until neutral pH was reached.

Regarding the resistances analysis, reversible resistance (R_{rev}) and irreversible resistance (R_{irrev}) have been calculated. The first one refers to the fouling that can be removed by water rinsing. By contrast, the second one includes the remaining fouling, which is caused by solutes both on membrane surface and inside membrane pores. R_{irrev} and R_{rev} were calculated by means of Eq. 1 and Eq. 2. Where, R_m is the initial membrane resistance, R_t is the membrane resistance at the end of the fouling step and J_{wr1} is the membrane flux after first rinsing step.

$$R_{irrev} = \frac{\Delta P}{\mu \cdot J_{wr1}} - R_m \quad (1)$$

$$R_t = R_{rev} + R_{irrev} + R_m \quad (2)$$

It is important to remark that when the initial permeability value of the membranes was not recovered at least in a 95%, at the end of the experiment an additional cleaning step with NaOH solution was carried out for a total membrane cleaning.

Finally, each experiment (initial permeability, fouling, cleaning and final permeability) was repeated at least twice, but if the results differed significantly, the experiment was repeated again and the mean values were reported.

2.5. Cleaning efficiency and permeability recovery calculation

Cleaning efficiency (CE) of the cleaning procedure with US as well as without US was calculated by means of the equation (Eq. 3) defined by (Matzinos and Álvarez 2002):

$$CE\ (\%) = \frac{R_t - R_c}{R_t - R_m} \times 100 \quad (3)$$

Where, R_c is the membrane resistance after the second rinsing step. Resistances were calculated from Darcy's law equation as previously described in (Luján-Facundo et al., 2013).

2.6. Zeta potential measurement

Zeta potential of the different fouling solutions at different pH values were measured by Zetasizer Nano ZS90 (Malvern Instruments, United Kingdom). Five different pH values were measured to determine the isoelectric point of the solution and to study the influence of calcium concentration increase on the solution charge.

2.7. Ultrafiltration modeling

The classical Hermia's model was applied to describe the reduction of flux during constant pressure filtration process based on the blocking laws and cake filtration (Hermia, 1982). This model was then modified by (Field et al., 1995) for cross-flow configuration according to the Eq. 4:

$$\frac{-dJ}{dt} = K \times (J - J_{ss}) \times J^{2-n} \quad (4)$$

Where *n* indicates the type of fouling, J_{ss} represents the steady-state permeate flux and *K* is the model constant depending on the fouling phenomenon. When n is 2 (complete pore blocking), it is assumed that solute molecules form a monomolecular layer on the membrane surface and each solute molecule arriving at the membrane surface lead to a complete pore blocking. If n takes a value of 1.5 (standard model blocking), solute molecules that are smaller than membrane pores can penetrate inside the membrane pores and block the inner pore walls. When n is 1 (intermediate fouling), it is considered that solutes cannot pass through membrane porous and are deposited on previously settled molecules. Finally, if the value of n is 0 (cake fouling), a cake layer is formed over the membrane surface due to solute molecules do not enter inside the membrane pores because solute molecules are larger than the membrane pores (Carbonell-Alcaina et al., 2016).

3. Results

3.1. Zeta potential study

Zeta potential gives a measure of the charge of the particles in the whey. In this way, zeta potential data may be important to explain membrane fouling. The evolution of the

zeta potential with the pH for the 5 different fouling solutions described in Table 1 was plotted in Fig.1. The pH value at which the zeta potential is zero, and particles charge in whey changes, is called isoelectric point. As it can be observed in Fig.1, there were no differences in the isoelectric point among the solutions with different concentration of $CaCl_2$ since for all the cases the isoelectric point was around 4.3. Thus, the increase in calcium concentration did not affect the isoelectric point. In this way, Almécija et al. (2007) published that whey proteins have an isoelectric point between 4.5 and 5.35 and (Lecoeur et al., 2010) reported a value between 4 and 5.

On the other hand, at pH 7.5 (pH of the fouling solutions during the fouling step) all the fouling solutions had a negative charge. However, as calcium concentration increases the charge of the fouling solution decreases (-23.9 mV for fouling solution 1 and -12.9 mV for fouling solution 5). The presence of calcium reduced zeta potential value since the adsorption of calcium ions onto the proteins particles could moderate the negative surface charge of the colloids (Dukhin and Parlia, 2014; Yang et al., 2010).

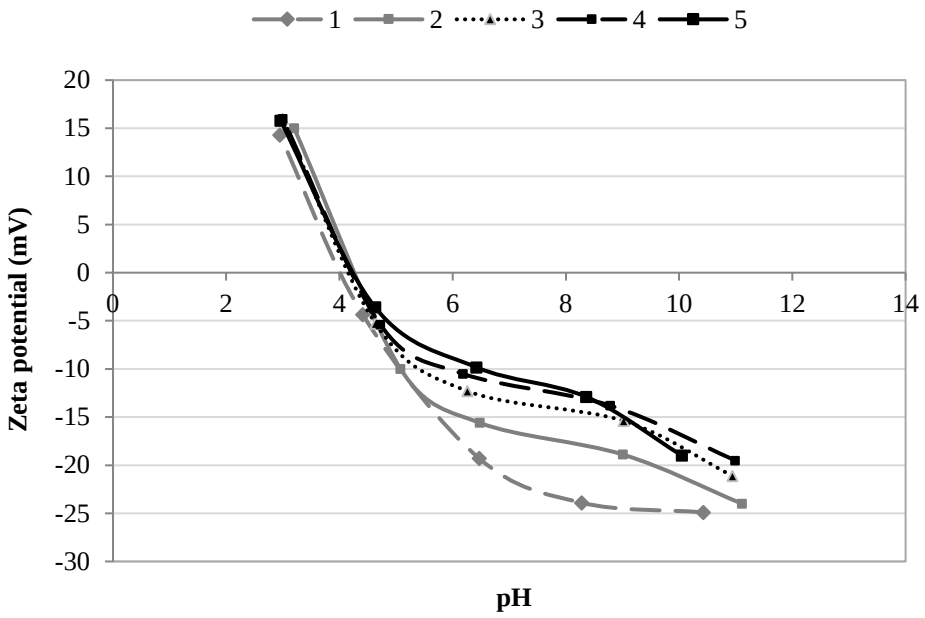


Figure 1: Evolution of zeta potential with pH for the five fouling solutions tested.

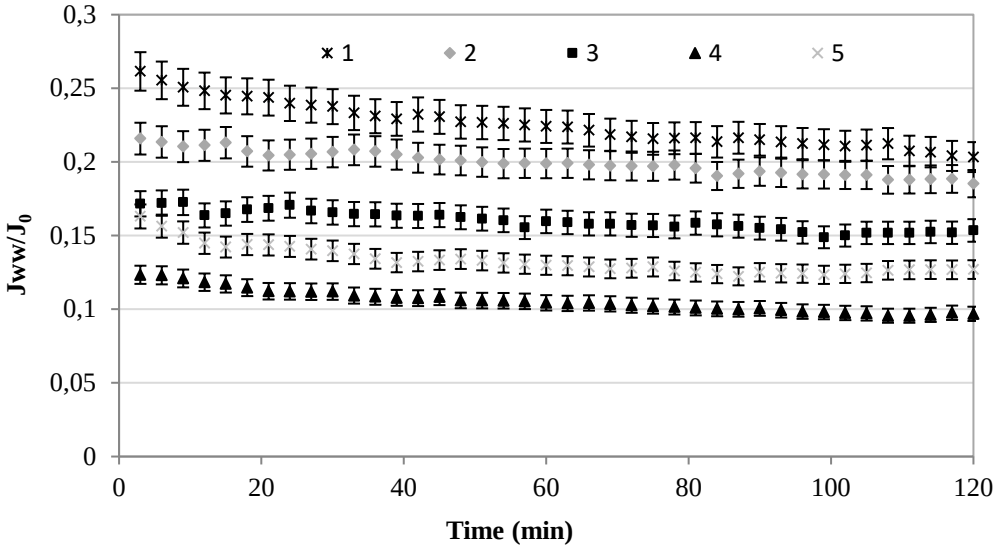
3.2. Influence of the calcium content on the membrane fouling

3.2.1. Normalized membrane flux

Fig. 2 illustrates the evolution of the relative permeate flux (J_{ww}/J_0) of both membranes (UH030 and UP005) at the five different fouling solutions tested summarized in Table 1. J_{ww} represents the membrane flux during the fouling step and J_0 is the membrane initial water flux. It is observed that, in all the experiments, relative permeate flux decreased from the beginning of the fouling step because of the membrane fouling. This behavior is commonly observed in UF processes.

Fig. 2 also shows that relative permeate flux decreases when the calcium content increases in the fouling solution. As it was expected, calcium content had a paramount importance in the fouling of both membranes. For each fouling solution, the relative permeate flux had the lowest values, in all the cases, for the membrane with the largest pore size (UH030). This fact corroborates that UH030 membrane is more prone to fouling than UP005 due to the membrane material characteristics and pore size. This pore size may cause that some molecules can be adsorbed inside the pores (Luján-Facundo et al., 2016, 2015, 2013).

a)



b)

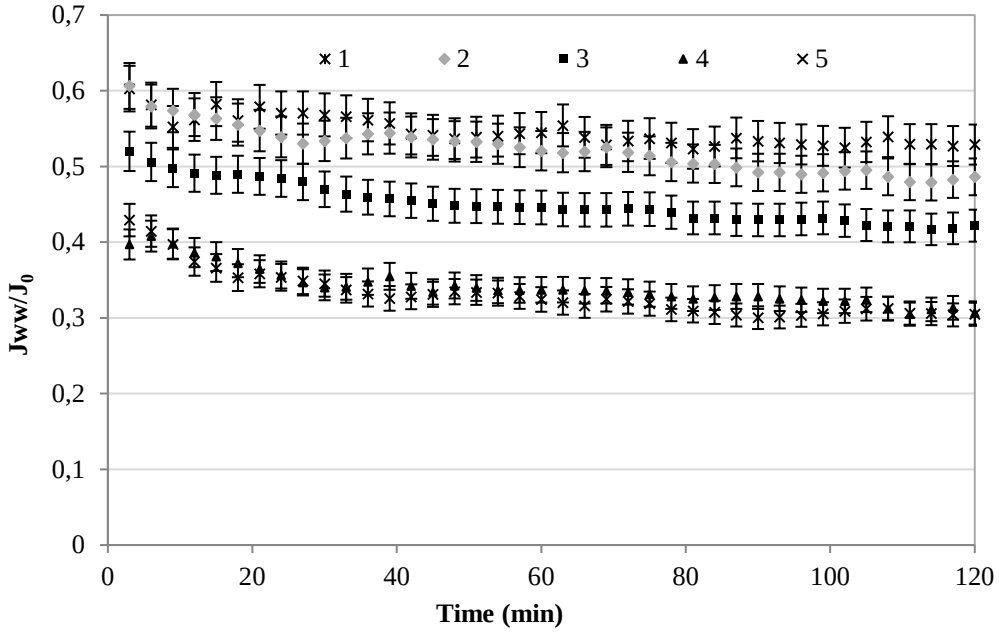


Figure 2: Evolution of relative permeate flux with time during the fouling step for a) UH030 and b)UP005.

3.2.2. Resistances analysis

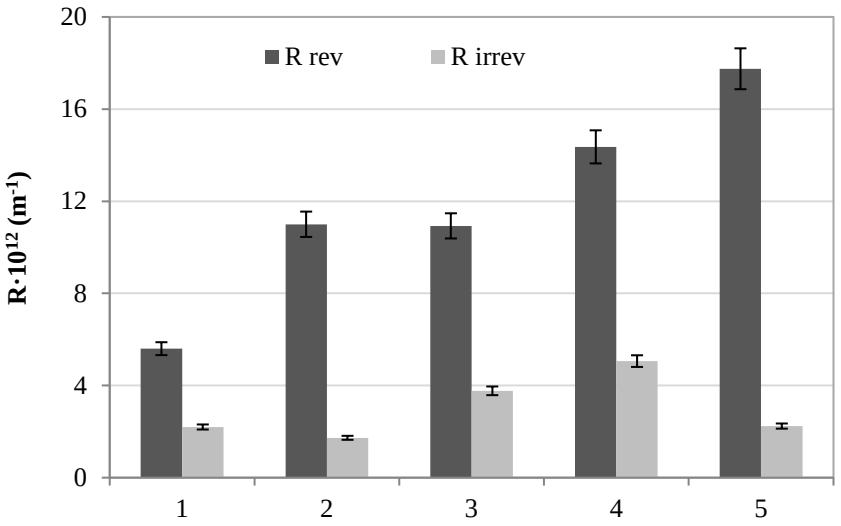
To study the fouling type of the two membranes with the increase of calcium concentration in the feed solution, membrane resistances R_{rev} and R_{irrev} were calculated as it was explained in the materials and methods section. Fig. 3 shows the R_{rev} and R_{irrev} for each test for UH030 and UP005 membranes. It can be observed that for all the solutions, reversible fouling prevails for UH030, meanwhile irreversible fouling is more pronounced for UP005 than for UH030.

It is also noticed that for UH030 membrane as calcium concentration increases the percentage of reversible resistance over irreversible resistance also increases (with values of 71.79% for test number 1 and 88.79% for test number 5). By contrast, for UP005 membrane, for increasing calcium concentration the irreversible resistance increases over reversible resistance (with values of 42.81% for test number 1 and 85.83% for test number 5). This phenomenon is related with the different membrane cut off and membrane properties. The irreversible adhesion of proteins can occur easier on the membrane with smaller pore size (UP005). Qu et al. (2014) reported that tighter UF membranes would be more affected than wider membranes by irreversible fouling.

As it was commented above, the presence of calcium increased the membrane fouling of both membranes. This can be explained by two reasons: calcium precipitation

(Ramachandra Rao, 2002) and formation of bridges between the proteins and the membrane, as well as among protein molecules (Cheryan, 1998).

a)



b)

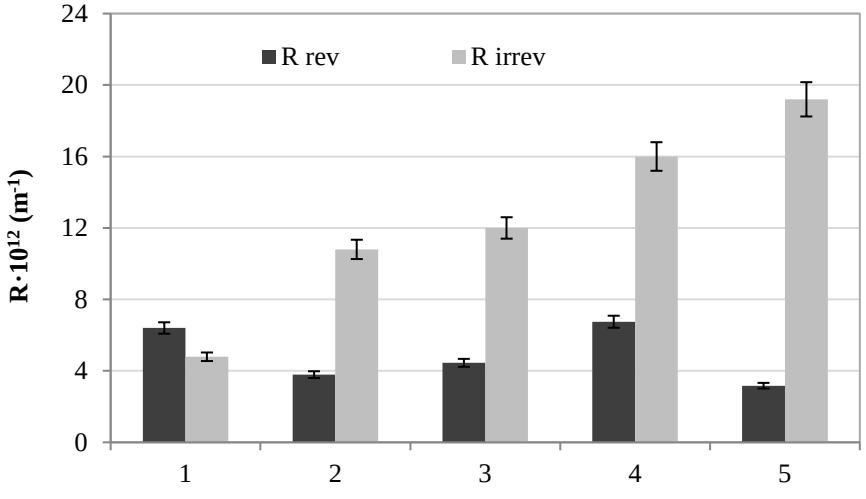


Figure 3: Reversible and irreversible resistance for: a) UH030 membrane and b) UP005 membrane.

3.2.3. Modeling results

Table 2 shows the fitting accuracy (R^2) for each fitting model, membrane and fouling solution tested. The models with the best fitting accuracy were highlighted in bold for each membrane and fouling solution tested. For UH030 membrane, it seems clear that the best fitting model was the cake layer model since for every experiment (except for test 5) the best fitting accuracy was achieved. This indicates that for UH030 membrane the predominant fouling mechanism was the cake layer formation. By contrast, for UP005 membrane, the experimental dates were adjusted better for the intermediate blocking model and for the complete blocking model, depending on the test, and with similar R^2. However, especially for UP005 membrane, the three different models studied had similar R^2 values. This implies that for UP005 membrane, the fouling mechanisms were both, blocking and cake layer models. In addition, it is important to consider that both models (blocking and cake layer) suppose that the fouling is external and occur over the membrane surface (Brião and Tavares, 2012).

Table 2: Measures of fit (R^2) of Hermia's models for a) UH030 and b) UP005.

a)

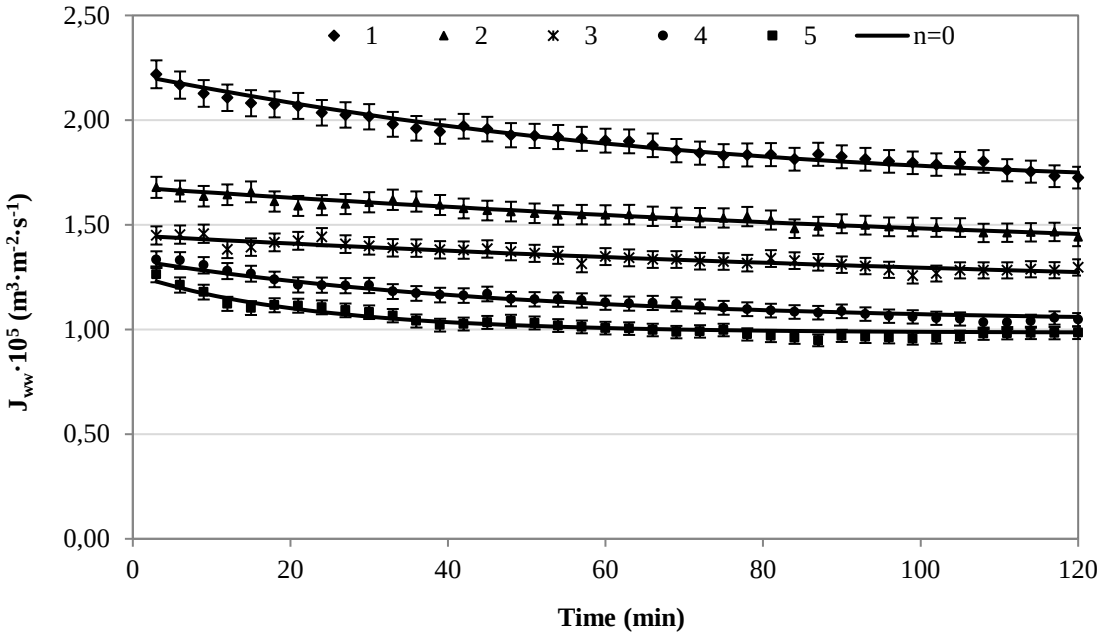
Test	Membrane	Complete blocking (n =2)	Intermediate blocking (n = 1)	Cake layer (n = 0)
1	UH030	0.980	0.979	**0.983**
2	UH030	0.922	0.920	**0.957**
3	UH030	0.884	0.880	**0.910**
4	UH030	0.976	0.880	**0.981**
5	UH030	0.953	**0.955**	0.952

b)

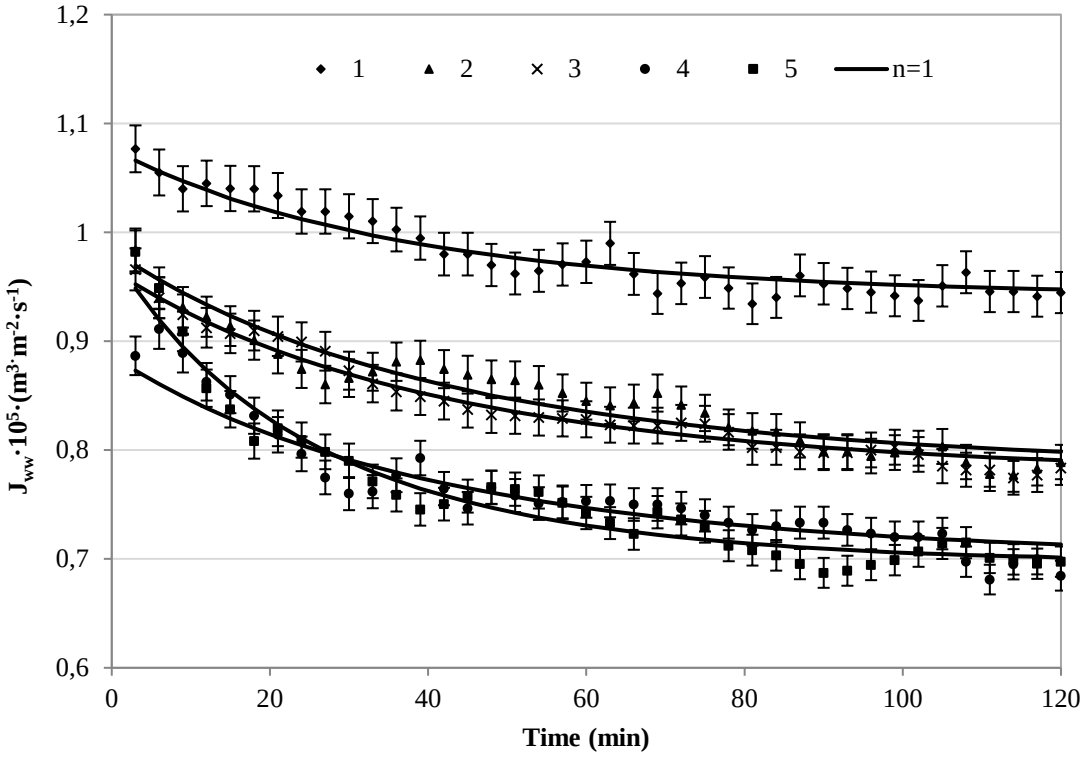
Test	Membrane	Complete blocking (n =2)	Intermediate blocking (n = 1)	Cake layer (n = 0)
1	UP005	**0.942**	0.941	0.906
2	UP005	0.910	**0.911**	0.901
3	UP005	**0.978**	0.977	0.977
4	UP005	0.920	0.924	**0.925**
5	UP005	0.950	**0.956**	0.868

In this way, Fig. 4 shows the comparison between the experimental permeate flux during the UF experiments and the permeate flux predicted by the Hermia's model for the best fitting accuracy (according with the results shown in Table 2) for each membrane and fouling solution tested. As expected, as calcium concentration increased, flux values were lower because of the membrane fouling. These results were in concordance with the results commented above in the normalized membrane flux (Section 3.2.1) and resistances analysis (Section 3.2.2).

a)



b)



c)

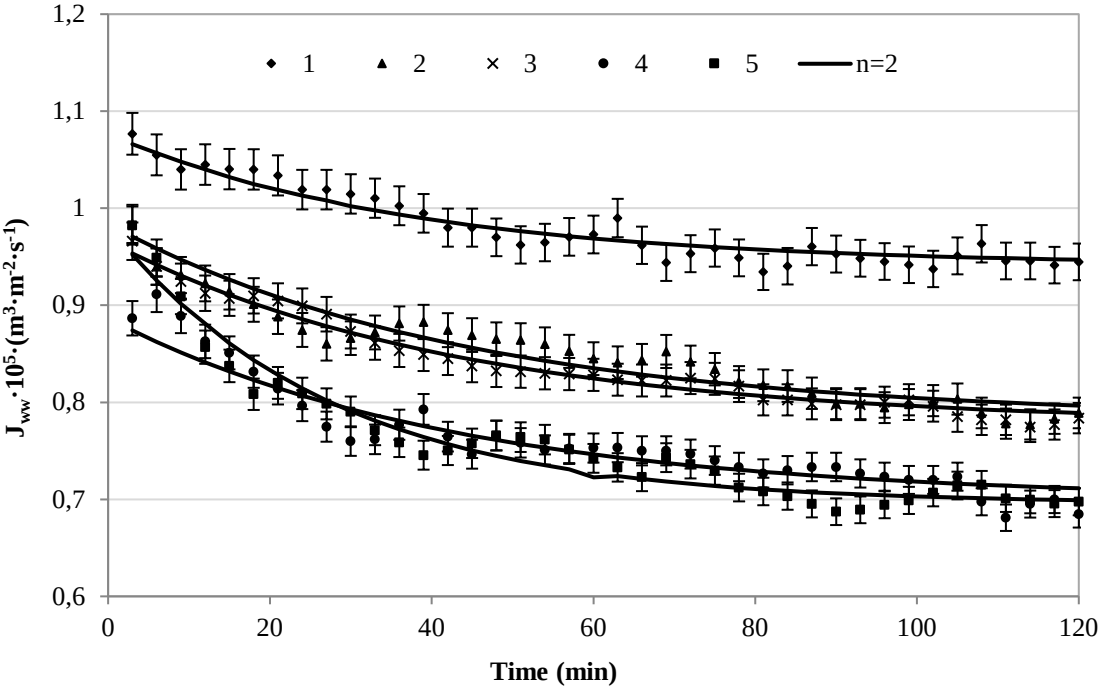


Figure 4: Comparison between the experimental permeate flux and the permeate flux predicted by the Hermia's model for a) UH030 and cake layer model, b) UP005 and intermediate model blocking and c) UP005 and complete model blocking.

Table 3 shows the values of the fitted parameters of Hermia's models for the fouling experimental data. Taking into account the definitions of the parameters of Hermia's models (*k*), as k increases the degree of membrane fouling also increases. Thus, it is observed in Table 3 that in general terms, *k* value increased with the calcium concentration in the solution. Especially, for both membranes, the highest *k* parameter value was achieved for the test number 5, in which the calcium concentration is the highest.

The fitting accuracy of the standard blocking model (n=1.5) was very low for all the experiments. For this reason, this model was not considered and the results were not shown. This could be related with the fact that solute molecules were larger than membrane pores (Renylat WPC solution had a mean diameter of 971.08 nm (Luján-Facundo et al., 2016), and they cannot penetrate inside the porous structure, as this model assumes. Similar results were reported by (Corbatón-Báguena et al., 2015), who also studied the membrane fouling of UH030 and UP005 for different protein model solutions.

Table 3: Fitted parameters of Hermia's models for a) UH030 and b) UP005.

a)

		Complete blocking (n =2)	**Intermediate blocking (n = 1)**	**Cake layer (n = 0)**
Test	**Membrane**	**k_c (s^{-1})**	**k_i (m^{-1})**	**$k_{gl} \cdot 10^{-6}$ ($s \cdot m^{-2}$)**
1	UH030	879.33	967.76	19.80
2	UH030	1,073	1,130	7.04
3	UH030	1,225	1,283	3.34
4	UH030	1,789	1,283	21.10
5	UH030	3,316	3,722	44.66

b)

		Complete blocking (n =2)	**Intermediate blocking (n = 1)**	**Cake layer (n = 0)**
Test	**Membrane**	**k_c (s^{-1})**	**k_i (m^{-1})**	**$k_{gl} \cdot 10^{-6}$ ($s \cdot m^{-2}$)**
1	UP005	2,606	2,463	10.40
2	UP005	2,280	2,515	25.90
3	UP005	2,386	2,607	24.58
4	UP005	2,615	2,874	32.75
5	UP005	3,740	4,318	98.02

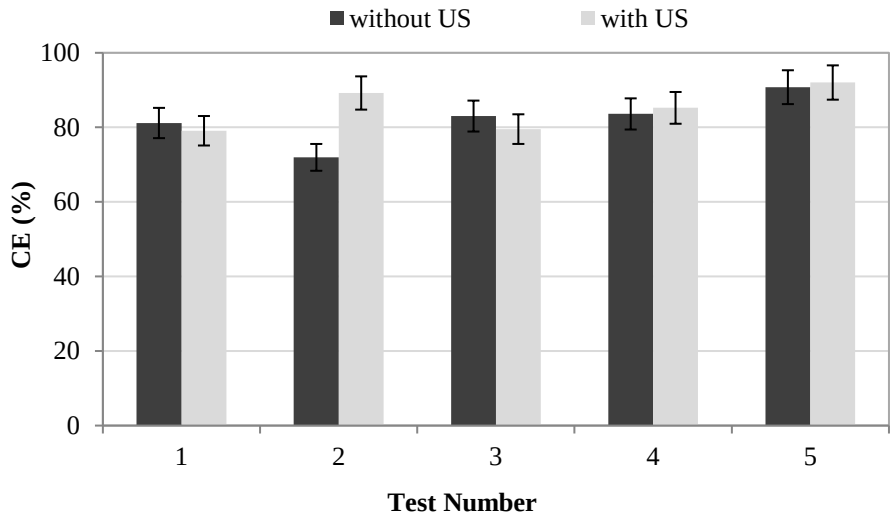
3.3. Effect of US on cleaning efficiency

Fig. 5 shows the values of CE obtained with and without US for UH030 and UP005 membrane. The average value of CE enhancement is 5.47% and 17.23% for UH030 and UP005 membranes. It is observed that as calcium concentration increases, the CE values of UP005 membrane decrease, that is, calcium concentration affects the UP005 cleaning (with and without US). By contrast, for UH030 membrane, the presence of calcium in the feed solution does not affect the membrane cleaning (with and without US) since the CE values are very similar. Furthermore, the difference between applying or not applying US was more significant for the membrane with lower pore size (UP005), which is related to the fact that without US the lowest CE were achieved.

As it was commented in the resistances analysis (Section 3.2.2), UH030 membrane had higher reversible fouling than UP005 membrane. For these reason, UH030 membrane achieved higher values of cleaning efficiency with and without US. This membrane presented a type of fouling much more reversible than UP005 membrane.

US application was effective because for almost every test it was achieved higher CE values with US than without US. In addition, it has been demonstrated (Muthukumaran et al., 2004) that the combination in the cleaning step between chemical agents (like NaOH solution) and US is effective since both mechanisms act synergistically. Whereas chemical agents weakens the binds between foulant and membranes, US help to loosen this molecules from the membrane and the turbulence generated in the fluid by the sonication increases the transport of these foulant molecules. In this way, Maskooki et al. (2008) applied US to clean PVDF membranes employed in the dairy industry. Results demonstrated that US application with EDTA at low concentrations (1-3 mM) was effective to clean the membranes achieving CE improvement values about 8%.

a)



b)

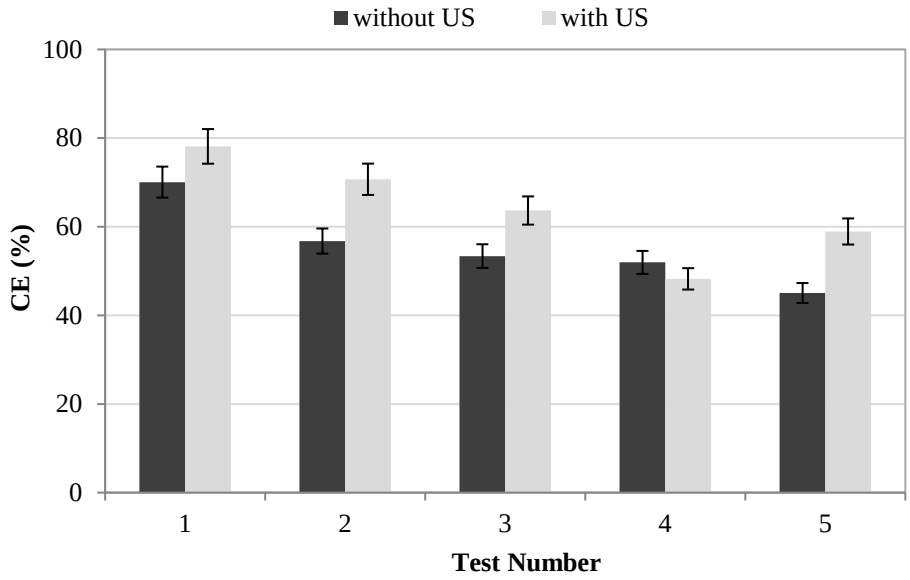


Figure 5: CE with and without US for a) UH030 membrane and b) UP005 membrane.

3.4. Analysis of US application cost

The cleaning procedure by means of US is environmental friendly since chemical products can be saved and the energy requirements are low because would only be applied during the chemical cleaning for the enhancement of the CE. In order to verify that the US application was economically feasible, an economical study has been performed to compare the chemical cleaning procedure with the US application.

The membrane supplier recommends carrying out at least a daily cleaning taking into account the characteristics of the membrane and the feed solution processed in the dairy industry. Thus, if it is assumed that the UF plant is working 8 hours, the cost will be calculated for the cleaning step for a daily operation. According to (Gutierrez, 2013), the recovery percentage of permeate stream is about 75% of total feed flow. In addition, it is obtained a protein concentrated between 30-40%. Nevertheless, (Bylund, 1996) published that the recovery percentage of permeate stream is about 83% of total feed

flow and the protein concentrated of 35%. In this case, it has been chosen as a reference (Gutierrez, 2013) because it is the most recent reference among the found ones.

As it was mentioned in the introduction section, 9 kg of cheese whey per 1 kg of cheese production are generated. Thus, assuming a cheese production around 8,800 kg per day, 79,200 kg of cheese whey would be generated. When this sub-product is filtered, it is obtained a permeate flow around 7.5 m^3/h. Van der Bruggen et al. (2001) reported that the cost associated to the chemical products is between 0.02 and 0.025 € per m^3 of permeate. Taking into account that NaOH is an economic product, the daily cost of the cleaning step it is shown in Eq. 5:

$$\text{Costs (NaOH)} = 0.02\ €\cdot m^{-3} \times 7.5\ m^3_{permeate}\cdot h^{-1} \times 8\ h = 1.2\ € \quad (5)$$

With regard to US equipment, it was decided installed a US equipment supplied by Hielscher (UIP4000), with a power of 4,000 W and frequency of 20 kHz. The selection was made on the basis of the required power and frequency. Regarding the power, the required power was the one used in the experimental tests per volume unit of the cleaning solution (power of 300 W and a cleaning bath of 10 liters, $30W\cdot l^1$). With respect to the frequency chosen in this study (20 kHz), the selected equipment operates just at this frequency. This unit has an energy consumption of 4 kW·h

Cleaning time is about 30 minutes, depending on the fouling degree and the size plant (D'Souza and Mawson, 2005). In this way, Guadix et al. (2004) reported that most chemical cleaners complete their action between 30-60 min. For 30 minutes of cleaning time and taking into account that energy cost in Spain is about 0.14 $€\cdot(kW\cdot h)^{-1}$, the energy cost due to energy consumption during 30 minutes is about 0.28 €. With respect to energy consumption associated to chemical cleaning solutions pumping, according to (Ali et al., 2005), the energy consumption in a membrane plant is around 0.04 kW·h per m^3 of feed solution pumped to the system and per bar of applied pressure. However, it is not considered this cost due to energy consumption is exactly the same with and without US application, in other words, it has not influence in the cost comparative.

In this way, the operational cost due to US equipment energy consumption (during 30 minutes) and due to chemical compounds it is summarized in Table 4.

Table 4: Analysis of costs.

Cleaning procedure	Daily cost (€)	Cost (€) assuming that plant is operating 222 days per year
NaOH	1.20	266.40
NaOH with US	1.48	328.56

Although also it must be consider the investment cost due to US equipment, according to (Muthukumaran et al., 2004), the major cost associated with US equipment is due to electricity supply. In addition, the cost are for 30 minutes of cleaning operation time but with US application could be achieved the same results with only 10 minutes of cleaning operation time (Shi et al., 2014). It can be concluded that the US employment could also be a feasible technique since an economical point of view.

Conclusions

UF processes applied to dairy industry are limited by their fouling. In this article, fouling and cleaning of UF membranes fouled with WPC solution has been studied.

Concerning to the membrane fouling, UH030 membrane was more prone to fouling than UP005, which was mainly due to the membrane material characteristics. When calcium concentration in the feed increased, fouling of both membranes was more severe. It has to be highlighted that for UP005 membrane the effect of adding calcium chloride to the WPC was to increase the irreversible fouling.

After applying the Hermia's models, the fluxes of the solution tested can be properly fitted according to the cake layer model. Nevertheless, neither of the model tested defined accurately the behavior of the UF process with all the tested solutions.

The application of US to the chemical cleaning solution improved the membrane cleaning efficiency in 5.47% and 17.23% for UH030 membrane and UP005 membrane. The application of US can be an important tool for the enhancement of the CE especially when irreversible fouling prevails, which occurs in the case of the UP005 membrane. Finally, the analysis of US application cost showed that the additional cost of US is very low; therefore this is a promising way of improving in a sustainable way the application of UF to cheese whey.

Acknowledgement

This work was supported by the Spanish Ministry of Science and Innovation (CTM 2010-20.186).

References

Ali, N., Mohammad, A.W., Ahmad, A.L., 2005. Use of nanofiltration predictive model for membrane selection and system cost assessment. Sep. Purif. Technol. 41, 29–37.

Almécija, M.C., Ibáñez, R., Guadix, A., Guadix, E.M., 2007. Effect of pH on the fractionation of whey proteins with a ceramic ultrafiltration membrane. J. Memb. Sci. 288, 28–35.

Alventosa-deLara, E., Barredo-Damas, S., Alcaina-Miranda, M.I., Iborra-Clar, M.I., 2014. Study and optimization of the ultrasound-enhanced cleaning of an ultrafiltration ceramic membrane through a combined experimental-statistical approach. Ultrason. Sonochem. 21, 1222–1234.

Bhattacharjee, S., Ghosh, S., Datta, S., Bhattacharjee, C., 2006. Studies on ultrafiltration of casein whey using a rotating disk module: effects of pH and membrane disk rotation. Desalination 195, 95–108.

Bylund, G., 1996. Manual de industrias lácteas, Suecia.

Carlini, M., Castellucci, S., Moneti, M., 2015. Biogas Production from Poultry Manure and Cheese Whey Wastewater under Mesophilic Conditions in Batch Reactor. Energy Procedia 82, 811–818.

Carbonell-Alcaina, C., Corbatón Báguena, M.J., Álvarez-Blanco, S., Bes-Pia, M.A., Mendoza-Roca, J.A., Pastor-Alcañiz, L., 2016. Determination of fouling mechanisms in polymeric ultra fi ltration membranes using residual brines from table olive storage wastewaters as feed. J. Food Eng. 187, 14–23.

Cassini, A.S., Tessaro, I.C., Marczak, L.D.F., Pertile, C., 2010. Ultrafiltration of wastewater from isolated soy protein production: A comparison of three UF membranes. J. Clean. Prod. 18, 260–265.

Cheryan, M., 1998. Ultrafiltration and Microfiltration Handbook.

Chi-Chuan K., Divine Angela, D. G., Kim Katrina P.R., de Luna, M.D.G., 2016. Ultrasonic cleaning of polytetrafluoroethylene (PTFE) membrane fouled by natural organic matter (NOM). J. Memb. Sci. 497, 450–457.

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

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

D'Souza, N., Mawson, A.J., 2005. Membrane cleaning in the dairy industry: a review. Food Sci. Nutr. 45, 125–134.

Dukhin, A.S., Parlia, S., 2014. Measuring zeta potential of protein nano-particles using electroacoustics. Colloids Surf. B. Biointerfaces 121, 257–63.

Field, R.W., Wu, D., Howell, J.A., Gupta, B.B., 1995. Critical flux concept for microfiltration fouling. J. Memb. Sci. 100, 259–272.

Gésan, G., Daufin, G., Merin, U., 1995. Performance of whey crossflow microfiltration during transient and stationary operating conditions. J. Memb. Sci. 104, 271-281.

Guadix, A., Sørensen, E., Papageorgiou, L.G., Guadix, E.M., 2004. Optimal design and operation of continuous ultrafiltration plants. J. Memb. Sci. 235, 131–138.

Gutierrez, H., 2013. Obtención de derivados lácteos por ultrafiltración. Alimentaria 51–54.

Hermia, J., 1982. Constant pressure blocking filtration laws-application to powerlaw non-newtonian fluids. Inst. Chem. Eng 60, 183–187.

Juang, R.S., Lin, K.H., 2004. Flux recovery in the ultrafiltration of suspended solutions with ultrasound. J. Memb. Sci. 243, 115–124.

Lecoeur, M., Gareil, P., Varenne, A., 2010. Separation and quantitation of milk whey proteins of close isoelectric points by on-line capillary isoelectric focusing-electrospray ionization mass spectrometry in glycerol-water media. J. Chromatogr. A 1217, 7293–301.

Luján-Facundo, M.J., Mendoza-Roca, J.A., Cuartas-Uribe, B., Álvarez-Blanco, S., 2013. Ultrasonic cleaning of ultrafiltration membranes fouled with BSA solution. Sep. Purif. Technol. 120, 275–281.

Luján-Facundo, M.J., Mendoza-Roca, J.A., Cuartas-Uribe, B., Álvarez-Blanco, S., 2015. Evaluation of cleaning efficiency of ultrafiltration membranes fouled by BSA using FTIR–ATR as a tool. J. Food Eng. 163, 1–8.

Luján-Facundo, M.J., Mendoza-Roca, J.A., Cuartas-Uribe, B., Álvarez-Blanco, S., 2016. Ultrasonics Sonochemistry Cleaning efficiency enhancement by ultrasounds for membranes used in dairy industries. Ultrason. Sonochem. 33, 18–25.

Luján-Facundo, M.J., 2016. Influencia de la aplicación de ultrasonidos en la limpieza de membranas de ultrafiltración empleadas en separación de proteínas en la industria láctea.

Maskooki, A., Kobayashi, T., Mortazavi, S.A., Maskooki, A., 2008. Effect of low frequencies and mixed wave of ultrasound and EDTA on flux recovery and cleaning of microfiltration membranes. Sep. Purif. Technol. 59, 67–73.

Matzinos, P., Álvarez, R., 2002. Effect of ionic strength on rinsing and alkaline cleaning of ultrafiltration inorganic membranes fouled with whey proteins. J. Memb. Sci. 208, 23–30.

Mirabella, N., Castellani, V., Sala, S., 2014. Current options for the valorization of food manufacturing waste: a review. J. Clean. Prod. 65, 28-41.

Muthukumaran, S., Yang, K., Seuren, A., Kentish, S., Ashokkumar, M., Stevens, G.W., Grieser, F., 2004. The use of ultrasonic cleaning for ultrafiltration membranes in the dairy industry. Sep. Purif. Technol. 39, 99–107.

Nguyen, M., Reynolds, N., Vigneswaran, S., 2003. By-product recovery from cottage cheese production by nanofiltration. J. Clean. Prod. 11, 803-807.

Pal, P., Nayak, J., 2016. Development and analysis of a sustainable technology in manufacturing acetic acid and whey protein from waste cheese whey. J. Clean. Prod. 112, 59–70.

Parashar, A., Jin, Y., Mason, B., Chae, M., Bressler, D.C., 2016. Incorporation of whey permeate, a dairy effluent, in ethanol fermentation to provide a zero waste solution for the dairy industry. J. Dairy Sci. 99, 1–9.

Prazeres, A.R., Carvalho, F., Rivas, J., 2012. Cheese whey management: a review. J. Environ. Manage. 110, 48–68.

Qu, F., Liang, H., Zhou, J., Nan, J., Shao, S., Zhang, J., Li, G., 2014. Ultrafiltration membrane fouling caused by extracellular organic matter (EOM) from Microcystis aeruginosa: Effects of membrane pore size and surface hydrophobicity. J. Memb. Sci. 449, 58–66.

Ramachandra Rao, H.G., 2002. Mechanisms of flux decline during ultrafiltration of dairy products and influence of pH on flux rates of whey and buttermilk. Desalination 144, 319–324.

Shi, X., Tal, G., Hankins, N.P., Gitis, V., 2014. Fouling and cleaning of ultrafiltration membranes: A review. J. Water Process Eng. 1, 121–138.

V.B. Brião, Tavares, C.R.G., 2012. Pore blocking mechanism for the recovery of milk solids from dairy wastewater by ultrafiltration. Brazilian J. Chem. Eng. 29, 393–407.

Van der Bruggen, B., Everaert, K., Wilms, D., Vandecasteele, C., 2001. Application of nanofiltration for removal of pesticides, nitrate and hardness from ground water: rejection properties and economic evaluation. J. Memb. Sci. 193, 239–248.

Wang, J., Gao, X., Xu, Y., Wang, Q., Zhang, Y., Wang, X., Gao, C., 2016. Ultrasonic-assisted acid cleaning of nano fi ltration membranes fouled by inorganic scales in arsenic-rich brackish water. Desalination 377, 172–177.

Wang, L., Wang, Q., Li, Y., Lin, H., 2013. Ultrasound-assisted chemical cleaning of polyvinylidene fl uoride membrane fouled by lactic acid fermentation broth. Desalination 326, 103–108.

Yang, Q., Liu, Y., Li, Y., 2010. Control of protein (BSA) fouling in RO system by antiscalants. J. Memb. Sci. 364, 372–379.

Yorgun, M.S., Balcioglu, I.A., Saygin, O., 2008. Performance comparison of ultrafiltration, nanofiltration and reverse osmosis on whey treatment. Desalination 229, 204–216.