CLEANING EFFICIENCY ENHANCEMENT BY ULTRASOUNDS FOR MEMBRANES USED IN DAIRY INDUSTRIES

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Abstract

Membrane cleaning is a key point for the implementation of membrane technologies in the dairy industry for proteins concentration. In this study, four ultrafiltration (UF) membranes with different molecular weight cut-offs (MWCOs) (5, 15, 30 and 50 kDa) and materials (polyethersulfone and ceramics) were fouled with three different whey model solutions: bovine serum albumin (BSA), BSA plus CaCl₂ and whey protein concentrate solution (Renylat 45). The purpose of the study was to evaluate the effect of ultrasounds (US) on the membrane cleaning efficiency. The influence of ultrasonic frequency and the US application modes (submerging the membrane module inside the US bath or applying US to the cleaning solution) were also evaluated. The experiments were performed in a laboratory plant which included the US equipment and the possibility of using two membrane modules (flat sheet and tubular). The fouling solution that caused the highest fouling degree for all the membranes was Renylat 45. Results demonstrated that membrane cleaning with US was effective and this effectiveness increased at lower frequencies. Although no significant differences were observed between the two different US applications modes tested, slightly higher cleaning efficiencies values placing the membrane module at the bottom of the tank were achieved.

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

Membrane technologies are widely applied for many industrial applications, such as, dairy and food technology, pharmaceutical industry, chemical industry or waste water treatment [1]. The main advantages of membrane processes are low-energy requirements and high versatility. In particular, ultrafiltration (UF) is a membrane separation technique widely used in the food and dairy industry for milk dehydration, whey (a byproduct of cheese making) concentration and protein purification or fractionation [2]. However, the major problem of their application is permeate flux reduction due to the fouling of the membranes during the production stage.

In dairy industry, membrane fouling is caused by both organic and inorganic compounds (mainly proteins and ions) of the dairy solutions [3]. These molecules are deposited on the membrane surface or into the pores involving cake layer formation and pore plugging [4,5]. In addition, membrane fouling can be classified as hydraulically reversible and irreversible. The first one can be removed in the water rinsing step and the second one, which is more problematic, requires a chemical cleaning step [6].

For all these reasons, the overall process efficiency could be improved by applying an optimum cleaning procedure. Typically, the choice of the cleaning method depends on the module configuration, the membrane material and the nature of the fouling involved in the membrane process [7]. These methods can be classified into physical and chemical. Even though chemical cleaning methods are the most commonly used, they can cause severe membrane damage, often membrane replacement, chemical costs and chemical waste disposal due to the large quantities of chemicals products consumed in the cleaning step [8].

Consequently, alternative cleaning methods are continually under development. Thus, the use of ultrasonic application for membrane cleaning is a promising technique as other authors have recently reported [8,9]. Particularly, Muthukumaran et al. [10] studied the effect of US application and sonication time on cleaning polysulfone (PS) flat sheet UF membranes. They reported that US were effective but cleaning efficiency was not affected by sonication time. Regarding ceramic membranes, Popović et al. [7] studied the effect of US on cleaning ceramic UF membranes fouled with proteins. They concluded that US were more effective combined with detergent solutions than with alkali solutions [7]. In addition, US were also effective to clean membranes fouled by other substances and employed for other applications. For example, Alventosa de Lara et al. [1] studied the US application to clean ceramic UF membranes fouled with simulated textile waste water reporting that cleaning efficiency improves up to 25% with the use of US. On the other hand, Secondes et al. [11] combined US application with adsorption processes and UF. They demonstrated the capability of this hybrid system in removing emerging contaminants at high efficiencies. US irradiation enhanced the adsorption of the emerging contaminants onto activated carbon.
US mechanism consists of an agitation of the aqueous medium and creation of microbubbles by means of high-frequency sounds waves. When the collapse of the microbubbles occur, energy is released, which help to overcome the interactions between the foulant and the membrane, removing the foulant from the membrane surface or inside the pores [12,13]. Until now, ultrasounds have been tested submerging the membrane module inside the US bath [5,14–16]. In this study, as a novel aspect, US have been also tested applying them to the cleaning solution.

This work aims to study the effect of US application to clean organic and inorganic UF membranes fouled by model proteins solutions (BSA, BSA/CaCl₂ and commercial whey). In this work, two application modes were compared: US application in the membrane cleaning solution and in a bath where membrane module was submerged. Two chemical cleaning agents were tested in combination with US: NaOH and P3 Ultrasil 115 solution. The last one, is a specific surfactant specially recommended to remove organic foulants like proteins [17].

2. Materials and methods

2.1. Fouling and cleaning chemicals

To simulate feed streams from dairy industry, three model solutions were used to carry out the fouling step: BSA (66 kDa of molecular weight) supplied by Sigma Aldrich (Germany), BSA plus CaCl₂ (Panreac, Spain) and whey protein concentrate solution (Renylat 45) from Reny Picot (Spain). The first solution tested was BSA with a concentration of 1% w/w. The second one was a mixture between BSA and CaCl₂ with a concentration of 1% w/w and 0.6% w/w in calcium, respectively. The last one was a Renylat 45 solution with a concentration of 2.22% w/w. Renylat 45 composition was described in a previous work [18]. Fouling chemicals were dissolved in deionized water and solutions were stored at 4°C to maintain them in optimal conditions.

Particle size distribution of Renylat 45 was measured with Zetasizer Nano ZS from Malvern.

The cleaning agents used were a surfactant P3 Ultrasil 115 and NaOH solution (Panreac, Spain). The first one is a specific surfactant to clean membranes used in the dairy industry. It was provided obtained from Ecolab (Spain) and the second one was supplied by Panreac (Spain).
2.2. Membranes

Four membranes of different cut-off, configuration and material were selected to carry out the experiments. In this way, two flat sheet polymeric membranes from Microdyn Nadir (Germany) and two monotubular ceramic membranes Inside Céram from Tami Industries (France) were tested. The criterion to select these membranes was to compare the influence of the membrane material and molecular weight cut-off (MWCO) in terms of protein rejection, membrane fouling and cleaning. Membrane MWCO were chosen with pore size between 1-100 nm to achieve high retention of proteins [2]. Table 1 summarizes the characteristics of these membranes.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Inside Céram 50 kDa</th>
<th>UH030</th>
<th>Inside Céram 15 kDa</th>
<th>UP005</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active layer</td>
<td>ZrO₂ / TiO₂</td>
<td>PESH*</td>
<td>ZrO₂ / TiO₂</td>
<td>PES*</td>
</tr>
<tr>
<td>Type</td>
<td>tubular</td>
<td>flat sheet</td>
<td>tubular</td>
<td>flat sheet</td>
</tr>
<tr>
<td>MWCO (kDa)</td>
<td>50 kDa</td>
<td>30 kDa</td>
<td>15 kDa</td>
<td>5 kDa</td>
</tr>
<tr>
<td>Water flux at 25°C (l/m²·h·bar)</td>
<td>&gt; 210</td>
<td>&gt; 180</td>
<td>&gt; 80</td>
<td>&gt; 71</td>
</tr>
<tr>
<td>Maximum operating temperature (°C)</td>
<td>300</td>
<td>95</td>
<td>300</td>
<td>95</td>
</tr>
<tr>
<td>pH range</td>
<td>0-14</td>
<td>0-14</td>
<td>0-14</td>
<td>0-14</td>
</tr>
<tr>
<td>Effective area (cm²)</td>
<td>35.81</td>
<td>100</td>
<td>35.81</td>
<td>100</td>
</tr>
</tbody>
</table>

*polietersulphone hydrophilic (PESH) and polietersulphone (PES)

2.3. UF plant

A UF laboratory plant from Orelis (France) was used to carry out the fouling and cleaning experiments. The main elements of the laboratory plant were: a feed tank solution with a capacity of 15 L, a volumetric pump, two manometers placed on the inlet and outlet of the membrane module, a system to regulate the temperature and a precision balance to measure gravimetrically the permeate flux. Depending on the US application mode, two different UF plant configurations were arranged (Fig. 1). The US equipment consists of an US generator and US bath supplied by TSD Machinery (USA). Two different membrane modules were employed. The first one was a Rayflow flat sheet module from Orelis (France) with capacity for two membranes of 100 cm² each one. The second one was a Carbosep tubular module from TAMI Industries (France) used for testing tubular inorganic membranes.
2.4. Experimental procedure

Experimental methodology includes the following stages: an initial deionized water flux measurement, a fouling step with the protein model solutions, a cleaning step and finally, measurement of water flux.
2.4.1. Water flux measurements and fouling step

The initial and final water flux measurements were performed to determine the membrane permeability before and after each experiment. Both water flux measurements and fouling experiments were carried out at a temperature of 25°C. Membranes were fouled with three different fouling solutions: BSA (1% w/w), BSA/CaCl₂ (1% w/w and 0.6% w/w in calcium) and Renylat 45 (2.22% w/w). Table 2 summarizes the experimental conditions applied for the experiments. All fouling tests were carried out at the same experimental conditions to evaluate and compare the different cleaning procedures studied, excepting cross flow velocity, which was different for organic and ceramic membranes since its value depended on the limitations of each membrane module.

Initial and final membrane filtration resistances (R_m and R_c, respectively) were calculated at the beginning or at the end of each test, as appropriate, by means of Darcy’s law Equation (Eq. 1).

\[
J = \frac{\Delta P}{\mu \cdot R_m}
\]  

Where, J is the initial or final membrane permeate flux, ΔP is the transmembrane pressure and μ is the water viscosity. In the same way, the membrane resistance at the end of the fouling step (R_t) was determined using Eq.1, replacing J by the membrane flux after the fouling step.

2.4.2. Cleaning experiments

The cleaning experiments included a first rinsing, a chemical cleaning (where US were applied in half of the tests) and a final rinsing. Cross flow velocity, duration of each step and transmembrane pressure in each cleaning step are described in Table 2.

Table 3 summarizes the experimental cleaning conditions for each test. The chemical cleaning step was carried out with NaOH solution and with P3 Ultrasil 115 solutions. It was decided to choose these two reagents to compare an alkali and a surfactant solution for the cleaning of UF membranes used in dairy industry. Even though other researchers [7,19] have considered higher temperatures and concentrations of chemical cleaning agents, in this study lower values of temperature and concentration have been tested to appreciate US improvements.

Temperature and concentration of cleaning solutions applied (Table 3) for ceramic membranes were higher than for polymeric membrane since inorganic membranes
seems to be more prone to fouling and materials are not damaged by these conditions. Surfactant concentrations (0.5 and 0.9% v/v) have been chosen according to surfactant manufacturer suggestions and taking into account the experimental conditions tested by other authors [7,20–22].

According to resistances calculation, reversible resistance \( R_{\text{rev}} \) includes surface fouling that can be removed by water. By contrast, irreversible resistance \( R_{\text{irrev}} \) concerns fouling both on membrane surface and inside membrane pores and it can be eliminated by chemical or physical methods. \( R_{\text{irrev}} \) and \( R_{\text{rev}} \) were calculated by means of Eq. 2 and Eq. 3, respectively. \( J_{\text{w1}} \) is the membrane flux after first rinsing step.

\[
R_{\text{irrev}} = \frac{\Delta P}{\mu} \cdot J_{\text{w1}} - R_m \tag{2}
\]

\[
R_t = R_{\text{rev}} + R_{\text{irrev}} + R_m \tag{3}
\]

Finally, if the initial permeability of the membranes was not recovered at least in a 95%, an extra cleaning procedure with P3 Ultrasil 115 solution was carried out for a total membrane cleaning.

**Table 2: Experimental conditions.**

<table>
<thead>
<tr>
<th>Stage</th>
<th>CFV (m·s(^{-1}))</th>
<th>TMP (bar)</th>
<th>Time (min)</th>
<th>Feed stream</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial water flux</td>
<td>2 3 1-3 90</td>
<td></td>
<td></td>
<td>Deionized water</td>
</tr>
<tr>
<td>Fouling</td>
<td>2 3 2 120 30</td>
<td></td>
<td></td>
<td>BSA / BSA plus CaCl(_2) / Renylat 45</td>
</tr>
<tr>
<td>First rinsing</td>
<td>2.2 4.2 1 30</td>
<td></td>
<td></td>
<td>Deionized water</td>
</tr>
<tr>
<td>Chemical cleaning</td>
<td>2.2 4.2 1 30</td>
<td></td>
<td></td>
<td>NaOH / Ultrasil</td>
</tr>
<tr>
<td>(with or without US)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Second rinsing</td>
<td>2 4.2 5</td>
<td></td>
<td></td>
<td>Deionized water</td>
</tr>
<tr>
<td>Final water flux</td>
<td>2 3 1-3 90</td>
<td></td>
<td></td>
<td>Deionized water</td>
</tr>
</tbody>
</table>
Table 3: Experimental cleaning conditions: a) flat sheet membranes and b) tubular membranes.

### a) Flat sheet membranes

<table>
<thead>
<tr>
<th>Test number</th>
<th>Feed stream</th>
<th>Cleaning agent</th>
<th>T (ºC)</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Renylat 45</td>
<td>P3 Ultrasil 115</td>
<td>35</td>
<td>0.5% v/v</td>
</tr>
<tr>
<td>2</td>
<td>BSA</td>
<td>P3 Ultrasil 115</td>
<td>35</td>
<td>0.5% v/v</td>
</tr>
<tr>
<td>3</td>
<td>BSA</td>
<td>NaOH</td>
<td>35</td>
<td>pH 11</td>
</tr>
<tr>
<td>4</td>
<td>BSA/CaCl₂</td>
<td>P3 Ultrasil 115</td>
<td>35</td>
<td>0.5% v/v</td>
</tr>
</tbody>
</table>

*T: temperature

### b) Tubular membranes

<table>
<thead>
<tr>
<th>Test number</th>
<th>Feed stream</th>
<th>Cleaning agent</th>
<th>T (ºC)</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Renylat 45</td>
<td>P3 Ultrasil 115</td>
<td>45</td>
<td>0.9% v/v</td>
</tr>
<tr>
<td>6</td>
<td>BSA</td>
<td>P3 Ultrasil 115</td>
<td>45</td>
<td>0.9% v/v</td>
</tr>
<tr>
<td>7</td>
<td>BSA</td>
<td>NaOH</td>
<td>45</td>
<td>pH 11</td>
</tr>
<tr>
<td>8</td>
<td>BSA/CaCl₂</td>
<td>P3 Ultrasil 115</td>
<td>45</td>
<td>0.9% v/v</td>
</tr>
</tbody>
</table>

*T: temperature

### 2.4.3. Ultrasounds application

To assist chemical cleaning step, US were applied in two different modes: submerging the membrane module in the US bath or generating US in the chemical cleaning solution (NaOH or P3 Ultrasil 115 solution). In the first one, in order to study the influence of the distance between the membrane module and the transducers, the membrane module was placed at the bottom of the US bath (0 cm) or at a distance of 3 cm from the bottom of the US bath. It is important to highlight that US were tested at a fixed nominal power of 300W and a frequency test was performed to choose the optimal frequency. Other authors [9,23–25] have reported that US are effective at low frequencies. For these reasons, the frequencies chosen to carry out the experiments were: 20 kHz, 25 kHz, 30 kHz and 38 kHz. Frequencies test was carried out with polymeric membranes (UH030 and UP005). The fouling solution chosen to perform the experiments was BSA (1% w/w) and cleaning test was carried out with NaOH solution at temperature of 25ºC and pH 10 (test A) and at temperature of 35ºC and pH 11 (test B). It is important to remark that for the frequency test US were applying to the cleaning solution. The rest of the experiments reported in this article were carried out at 20 kHz, which was the selected frequency as it was shown in the results section.
It is important to note that each test was carried out with and without US application under the same experimental conditions in order to evaluate the effect of US on the cleaning performance.

2.4.4. Evaluation of the cleaning efficiency and US improvement

The criterion employed to assess the cleaning procedure was the evaluation of the cleaning efficiency (CE). This parameter was calculated according Eq.4 defined by [26]:

\[
CE(\%) = \frac{R_t - R_c}{R_t - R_m} \times 100
\] (4)

Eq. 5 was used to evaluate the effect of the US application on the CE [14]:

\[
CE_{ENH}(\%) = \frac{CE_{with\ US} - CE_{without\ US}}{CE_{without\ US}} \times 100
\] (5)

3. Results

3.1. Membrane fouling

Fig. 2 shows the flux reduction in the fouling tests. Values were calculated dividing the final permeate flux by the initial flux measured using distilled water. It was observed that Renylat 45 was the feed stream that caused the highest membrane fouling (the highest flux decrease for all the membranes), followed by BSA/CaCl₂ solution and finally by BSA solution. As previously reported by Shi et al. [12], the presence of calcium in the feed solution increased membrane fouling since this cation can form a bridge between proteins and membrane, as well as among proteins. In addition, the heterogeneous composition of Renylat 45, with both salts and lactose, enhanced membrane fouling [27].
In a previous study [18], it was reported that the mean particle size of the Renylat 45 solution was 971.1 nm (much more higher than the other two fouling solutions). In this case, fouling solution size is an indicator of the particles aggregation degree. The heterogeneous composition of Renylat 45 leads to a higher particle size solution. Fig. 3 shows the particle size distribution for this solution (sample was measured three times, test 1, 2 and 3 as it can be observed in Fig. 3). It can be observed that the peak with the highest intensity corresponds with the above mentioned particle size.

On the other hand, Renylat 45 caused higher fouling for organic than for inorganic membranes. In this way, Hofs et al. [28] reported that fouling degree is higher for organic than for inorganic membranes, at least when membranes were fouled with lake water. In addition, this group of researchers concluded that the lower volume/area ratio, the more membrane fouling degree. Following this explanation, organic membranes had a lower volume/area ratio than inorganic membranes since they were tested in a flat sheet module.

For BSA and BSA/CaCl2 solutions, UH030 and Inside Céram 50 kDa were the membranes that presented the highest flux decrease. The main reason could be related with the molecular weight cut off of these membranes, since the pore size of both membranes are much closer to the BSA size (66 kDa). This was also observed by Qu et al. [29]. These authors fouled three PES membranes (with molecular weight cut-offs of 10, 30 and 100 kDa) with extracellular polymeric substances.

![Figure 2: Percentage flux reduction for all the membranes.](image-url)
3.2. US frequency selection.

As explained in section 2.4.3, four different frequencies (20 kHz, 25 kHz, 30 kHz and 38 kHz) have been tested to study the influence of this parameter on the membrane cleaning efficiency. The experiments were carried out at the same experimental conditions with and without US application. As it can be observed in Table 4, test A indicates that the optimum frequency was 25 kHz since the highest US improvement (14.7% and 35.3% for UH030 and UP005, respectively) was achieved. By contrast, according to the results from test B, the optimum frequency was 20 kHz for both membranes (5.3% and 12.7% for UH030 and UP005, respectively), what coincides with the results of other authors [9,23–25]. Thus, tests confirmed that US are more effective at low frequencies. Then, the use of high frequencies was discarded and it was decided to apply US at 20 kHz in the following experiments. The variation of US frequency may modify the interactions between the wave created and the fluid as well as the characteristics of the microbubbles formed. When low frequencies are applied, microbubbles created are larger than when high frequencies are employed, so their intense collapse may generate stronger vibrations which is the main reason of US enhancement [9,30].
Table 4: $C_{\text{ENH}}$ in the tests for frequency selection.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Test</th>
<th>20 kHz</th>
<th>25 kHz</th>
<th>30 kHz</th>
<th>38 kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>UH030</td>
<td>A</td>
<td>7.3</td>
<td>14.9</td>
<td>5.4</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>5.3</td>
<td>3.2</td>
<td>0</td>
<td>1.1</td>
</tr>
<tr>
<td>UP005</td>
<td>A</td>
<td>7.0</td>
<td>35.3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>12.7</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

3.3. Effect of US applied to the cleaning solution on cleaning efficiency

Fig. 4 shows the $C_E$ values with and without applying US to the cleaning solution for the four membranes tested (UH030, UP005, Inside Céram 50 kDa and Inside Céram 15 kDa). In general terms, US application improved the membrane cleaning since higher $C_E$ values with US than without US were achieved (at the same experimental conditions). The average $C_{\text{ENH}}$ for the eight tests using US and for each membrane were 3.8, 3.4, 3.4 and 6.1% for UH030, UP005, Inside Céram 50 kDa and Inside Céram 15 kDa, respectively. It is important to remark than Inside Céram 15 kDa achieved the highest improvement in terms of $C_E$ with US application since the lowest $C_E$ values without US was measured. In this way, membrane Inside Céram 15 kDa obtained the lowest $C_E$ values, especially for tests 6 and 7. This fact could be related with the degree of reversible/irreversible resistance, since Inside Céram 15 kDa was the membrane that had the highest irreversible fouling (25.8%, 77.6%, 60.6% and 79.0% for membranes UH030, UP005, Inside Céram 50 kDa and Inside Céram 15 kDa, respectively), i.e., the flux recovery was the lowest after water rinsing.

It has to be highlighted that the effect of US on membrane cleaning was easier to observe when NaOH was used as cleaning agent, since the $C_E$ values obtained with the NaOH solution were considerably lower than those obtained with P3 Ultrasil 115. This is the reason why the highest improvement in $C_E$ with US was achieved in tests number 3 and 7. NaOH solution behavior was worse than P3 Ultrasil 115 solution to clean UF membranes fouled with protein solutions at the operating conditions tested. Thus, the use of US could be required when cleaning procedures do not work properly, what is produced periodically at industrial scale during the membrane life.

The positive effect of the US on the membrane cleaning was mainly sonochemical. This was proved since no significant enhancement of the $C_E$ was obtained by applying US to distilled water in absence of NaOH (data not shown). In this way, US enhanced the hydrolysis of proteins at the pH of the cleaning solution. Denaturation of BSA may also be a mechanism enhanced by US for the detaching of adsorbed BSA from the membrane [31,32].
Similar results were obtained by Maskooki et al. [33], who applied US (after submerging the membrane module in a bath) for the cleaning of polyvinylidene fluoride UF membranes used in the dairy industry. The results demonstrated that US application with ethylenediaminetetraacetic acid at low concentrations (1-3 mM) was effective to clean the membranes and the reported improvement percentage with US was around 8%.

a)

b)
Figure 4: Cleaning efficiency applying US to the cleaning solution and US improvement for: a) UH030, b) UP005, c) Inside Céram 50 kDa and d) Inside Céram 15 kDa.
3.4. Effect of US submerging the membrane module

Table 5 shows the CE_{ENH} for the three different US application modes and for all the membranes. With regard to the results submerging the membrane module inside the US bath, for organic membranes, no significant differences were observed between the two different positions of the membrane module. However, UH030 membrane always achieved higher CE_{ENH} values than UP005 membrane (for both distances tested). This indicates that US were more effective for UH030 membrane than for UP005 membrane. The main reason could be that UH030 membrane had more reversible fouling than UP005 membrane. Similar results were reported by Kan et al. [8], who applied US in the cleaning step of polytetrafluoroethylene (PTFE) membranes previously fouled with natural organic matter (NOM). These researchers published that US were more effective to remove fouling from cake formation than from pore blocking.

Regarding to inorganic membranes, when US were applied submerging the membrane module inside the US bath, in the bottom of the tank (0 cm), it was achieved slightly higher US_{ENH} values than those obtained placing the membrane module at 3 cm from the bottom of the tank, especially for Inside Céram 50 kDa. Similar results were presented by Chen et al. [34], who demonstrated that US application to the filtration of a model solution with colloidal silica particles help to reduce the fouling caused over that particles in UF ceramic membranes. In addition, these authors demonstrated that the optimum distance between the membrane module and the transducers was 1.7 cm (minimum distance tested between membrane module and transducers).

<table>
<thead>
<tr>
<th>Test</th>
<th>Inside Céram 50 kDa</th>
<th>Inside Céram 15 kDa</th>
<th>UH030</th>
<th>UP005</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.7</td>
<td>0</td>
<td>15.2</td>
<td>12.5</td>
</tr>
<tr>
<td>2</td>
<td>6.8</td>
<td>50.7</td>
<td>3.8</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>30.4</td>
<td>74.3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>1.1</td>
<td>0</td>
<td>2.4</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test</th>
<th>Inside Céram 50 kDa</th>
<th>Inside Céram 15 kDa</th>
<th>UH030</th>
<th>UP005</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.9</td>
<td>0.4</td>
<td>14.7</td>
<td>10.8</td>
</tr>
<tr>
<td>2</td>
<td>5.5</td>
<td>29.1</td>
<td>3.9</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>18.8</td>
<td>78.6</td>
<td>15.4</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>0</td>
<td>2.4</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Table c)  

<table>
<thead>
<tr>
<th>Test</th>
<th>Inside Céram 50 kDa</th>
<th>Inside Céram 15 kDa</th>
<th>UH030</th>
<th>UP005</th>
</tr>
</thead>
<tbody>
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3.5. Comparison between the different US application modes.

Fig. 5 shows the CE including the effect of US application comparing the US application submerging the membrane module inside the US bath and applying US to the cleaning solution for UH030, UP005, Inside Céram 50 kDa and Inside Céram 15 kDa membrane. In general terms, for all the membranes, for tests 1, 2 and 4 (for organic membranes) and 5, 6 and 8 (for inorganic membranes), no significant differences were observed with the exception of tests number 1 and 5, in which US application submerging the membrane module does seem to be more effective than applying US to the cleaning solution (excepting for membrane Inside Céram 15 kDa). Tests number 1 and 5 was carried out with Renylat 45 solution. As previously commented, inorganic agents (as calcium cation) had influence on the membrane fouling. US application to the cleaning solution was less effective than submerging the membrane module in the US bath for removing calcium cations remaining on the membrane surface since the generated microbubbles remove more easily organic molecules (weekly bond to the membrane surface) than inorganic ones as calcium cations that drive to stronger interactions between proteins and membranes because of the bridges formed between them, as described in section 3.1. Similarly, Chen et al. [35] applied US to the cleaning of UF membranes fouled by natural organic matter and silica particles and they concluded that the presence of calcium cation increases fouling and reduces the effect of US on the CE.

When NaOH solution was tested (tests number 3 and 7), the CE values were quite low (in some cases lower than 60%). In this case, for the most fouled organic membrane according to the results described in section 3.1, US have to be applied either submerging the module at the minimum distance or to the cleaning solution.

Kyllönen et al. [36] reported that when the membrane module is submerged inside the US bath, there are energy losses due to the resistance that the membrane module offers. Thus, for industrial applications it has to be assessed if the energy loss and the disadvantage of submerging the modules makes up for the lower CE achieved when cations concentration is high.
Figure 5: CE comparing the different US application mode for: a) UH030, b) UP005, c) Inside Céram 50 kDa and d) Inside Céram 15 kDa.
4. Conclusions

The application of UF membranes in dairy industry is often limited by their fouling. US application enhances the membrane CE reducing the use of chemicals that can limit the membrane life.

The fouling experiments carried out at laboratory scale showed that calcium enhances membrane fouling in comparison with the fouling caused by protein solutions.

The application of US for membrane cleaning is more appropriate at low frequencies (20-25 kHz), since the use of higher frequencies does not improve membrane cleaning.

Although in some experiments the use of US seemed to be more efficient for ceramic membranes, it has not been found a relationship among US improvement, membrane material and molecular weight cut-off. Thus, $\text{CE}_{\text{ENH}}$ by US will depend on the fouling solution rather than on membrane material and molecular weight cut-off. The use of US applied to the cleaning solution leads to an improvement of membrane CE, what is especially remarkable when NaOH is used to clean the membrane due to its lower effect on fouling removal than Ultrasil. In general terms, no significant differences were observed applying US to the cleaning solution and submerging the module. However, the application of US to the cleaning solution can lead to lower $\text{CE}_{\text{ENH}}$ than those achieved submerging the module if the proteins are strongly bonded to the membrane due to high concentrations of cations like calcium.

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References


