

1 **CLEANING EFFICIENCY ENHANCEMENT BY ULTRASOUNDS FOR**
2 **MEMBRANES USED IN DAIRY INDUSTRIES**

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12 **Abstract**

13
14 Membrane cleaning is a key point for the implementation of membrane technologies in
15 the dairy industry for proteins concentration. In this study, four ultrafiltration (UF)
16 membranes with different molecular weight cut-offs (MWCOs) (5, 15, 30 and 50 kDa)
17 and materials (polyethersulfone and ceramics) were fouled with three different whey
18 model solutions: bovine serum albumin (BSA), BSA plus CaCl₂ and whey protein
19 concentrate solution (Renylat 45). The purpose of the study was to evaluate the effect of
20 ultrasounds (US) on the membrane cleaning efficiency. The influence of ultrasonic
21 frequency and the US application modes (submerging the membrane module inside the
22 US bath or applying US to the cleaning solution) were also evaluated. The experiments
23 were performed in a laboratory plant which included the US equipment and the
24 possibility of using two membrane modules (flat sheet and tubular). The fouling
25 solution that caused the highest fouling degree for all the membranes was Renylat 45.
26 Results demonstrated that membrane cleaning with US was effective and this
27 effectiveness increased at lower frequencies. Although no significant differences were
28 observed between the two different US applications modes tested, slightly higher
29 cleaning efficiencies values placing the membrane module at the bottom of the tank
30 were achieved.

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

39 **1. Introduction**

40

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

49

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

56

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

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66 Consequently, alternative cleaning methods are continually under development.
67 Thus, the use of ultrasonic application for membrane cleaning is a promising technique
68 as other authors have recently reported [8,9]. Particularly, Muthukumaran et al. [10]
69 studied the effect of US application and sonication time on cleaning polysulfone (PS)
70 flat sheet UF membranes. They reported that US were effective but cleaning efficiency
71 was not affected by sonication time. Regarding ceramic membranes, Popović et al. [7]
72 studied the effect of US on cleaning ceramic UF membranes fouled with proteins. They
73 concluded that US were more effective combined with detergent solutions than with
74 alkali solutions [7]. In addition, US were also effective to clean membranes fouled by
75 other substances and employed for other applications. For example, Alventosa de Lara
76 et al. [1] studied the US application to clean ceramic UF membranes fouled with
77 simulated textile waste water reporting that cleaning efficiency improves up to 25%
78 with the use of US. On the other hand, Secondes et al. [11] combined US application
79 with adsorption processes and UF. They demonstrated the capability of this hybrid
80 system in removing emerging contaminants at high efficiencies. US irradiation
81 enhanced the adsorption of the emerging contaminants onto activated carbon.

82 US mechanism consists of an agitation of the aqueous medium and creation of
83 microbubbles by means of high-frequency sounds waves. When the collapse of the
84 microbubbles occur, energy is released, which help to overcome the interactions
85 between the foulant and the membrane, removing the foulant from the membrane
86 surface or inside the pores [12,13]. Until now, ultrasounds have been tested submerging
87 the membrane module inside the US bath [5,14–16]. In this study, as a novel aspect, US
88 have been also tested applying them to the cleaning solution.

89
90 This work aims to study the effect of US application to clean organic and
91 inorganic UF membranes fouled by model proteins solutions (BSA, BSA/CaCl₂ and
92 commercial whey). In this work, two application modes were compared: US application
93 in the membrane cleaning solution and in a bath where membrane module was
94 submerged. Two chemical cleaning agents were tested in combination with US: NaOH
95 and P3 Ultrasil 115 solution. The last one, is a specific surfactant specially
96 recommended to remove organic foulants like proteins [17].

100 **2. Materials and methods**

103 **2.1. Fouling and cleaning chemicals**

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

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

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

122 2.2. Membranes

123

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

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Table 1: Membrane characteristics.

Characteristic	Inside Céram 50 kDa	UH030	Inside Céram 15 kDa	UP005
Active layer	ZrO ₂ / TiO ₂	PESH*	ZrO ₂ / TiO ₂	PES*
Type	tubular	flat sheet	tubular	flat sheet
MWCO (kDa)	50 kDa	30 kDa	15 kDa	5 kDa
Water flux at 25°C (l/m ² ·h·bar)	> 210	> 180	> 80	> 71
Maximum operating temperature (°C)	300	95	300	95
pH range	0-14	0-14	0-14	0-14
Effective area (cm ²)	35.81	100	35.81	100

134 *polietersulphone hydrophilic (PESH) and polietersulphone (PES)

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137 2.3. UF plant

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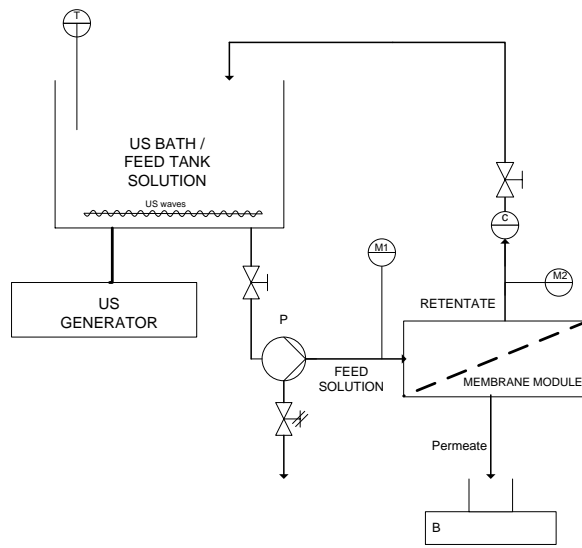
139 A UF laboratory plant from Orelis (France) was used to carry out the fouling and
140 cleaning experiments. The main elements of the laboratory plant were: a feed tank
141 solution with a capacity of 15 L, a volumetric pump, two manometers placed on the
142 inlet and outlet of the membrane module,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

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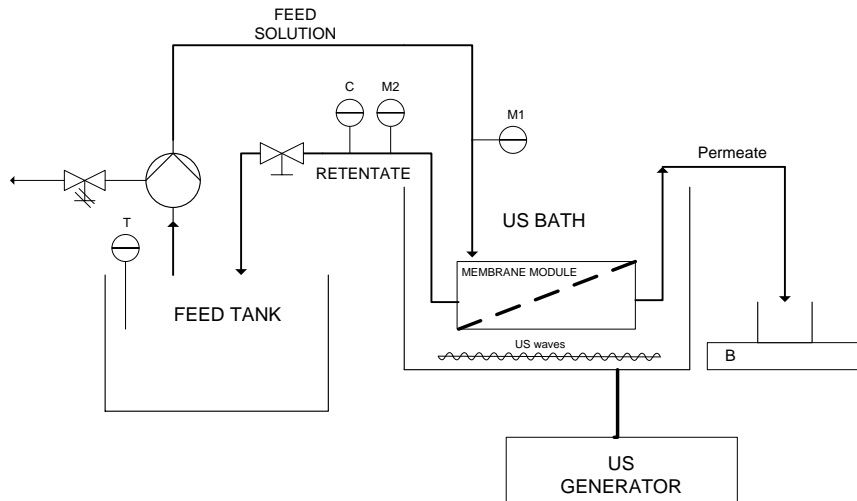
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165 2.4. Experimental procedure

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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.

173 **2.4.1. Water flux measurements and fouling step**
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176 The initial and final water flux measurements were performed to determine the
177 membrane permeability before and after each experiment. Both water flux
178 measurements and fouling experiments were carried out at a temperature of 25°C.
179 Membranes were fouled with three different fouling solutions: BSA (1% w/w),
180 BSA/CaCl₂ (1% w/w and 0.6% w/w in calcium) and Renylat 45 (2.22% w/w). Table 2
181 summarizes the experimental conditions applied for the experiments. All fouling tests
182 were carried out at the same experimental conditions to evaluate and compare the
183 different cleaning procedures studied, excepting cross flow velocity, which was
184 different for organic and ceramic membranes since its value depended of the limitations
185 of each membrane module.
186

187 Initial and final membrane filtration resistances (R_m and R_c , respectively) were
188 calculated at the beginning or at the end of each test, as appropriate, by means of
189 Darcy's law Equation (Eq. 1).
190

191
$$J = \frac{\Delta P}{\mu \cdot R_m} \quad (1)$$

192

193 Where, J is the initial or final membrane permeate flux, ΔP is the transmembrane
194 pressure and μ is the water viscosity. In the same way, the membrane resistance at the
195 end of the fouling step (R_t) was determined using Eq.1, replacing J by the membrane
196 flux after the fouling step.
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200 **2.4.2. Cleaning experiments**
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203 The cleaning experiments included a first rinsing, a chemical cleaning (where US
204 were applied in half of the tests) and a final rinsing. Cross flow velocity, duration of
205 each step and transmembrane pressure in each cleaning step are described in Table 2.
206

207 **Table 3 summarizes the experimental cleaning conditions for each test.** The
208 chemical cleaning step was carried out with NaOH solution and with P3 Ultrasil 115
209 solutions. It was decided to choose these two reagents to compare an alkali and a
210 surfactant solution for the cleaning of UF membranes used in dairy industry. Even
211 though other researchers [7,19] have considered higher temperatures and concentrations
212 of chemical cleaning agents, in this study lower values of temperature and concentration
213 have been tested to appreciate US improvements.
214

215 Temperature and concentration of cleaning solutions applied (Table 3) for ceramic
216 membranes were higher than for polymeric membrane since inorganic membranes

217 seems to be more prone to fouling and materials are not damaged by these conditions.
 218 Surfactant concentrations (0.5 and 0.9% v/v) have been chosen according to surfactant
 219 manufacturer suggestions and taking into account the experimental conditions tested by
 220 other authors [7,20–22].
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222 According to resistances calculation, reversible resistance (R_{rev}) includes surface
 223 fouling that can be removed by water. By contrast, irreversible resistance (R_{irrev})
 224 concerns fouling both on membrane surface and inside membrane pores and it can be
 225 eliminated by chemical or physical methods. R_{irrev} and R_{rev} were calculated by means of
 226 Eq. 2 and Eq. 3, respectively. J_{wr1} is the membrane flux after first rinsing step.
 227

$$228 \quad R_{irrev} = \frac{\Delta P}{\mu \cdot J_{wr1}} - R_m \quad (2)$$

$$231 \quad R_t = R_{rev} + R_{irrev} + R_m \quad (3)$$

232 Finally, if the initial permeability of the membranes was not recovered at least in a
 233 95%, an extra cleaning procedure with P3 Ultrasil 115 solution was carried out for a
 234 total membrane cleaning.
 235

236 **Table 2: Experimental conditions.**

Stage	CFV ($m \cdot s^{-1}$)		TMP (bar)	Time (min)	Feed stream
	Flat sheet	Tubular			
Initial water flux	2	3	1-3	90	Deionized water
Fouling	2	3	2	120	BSA / BSA plus $CaCl_2$ / Renylat 45
First rinsing	2.2	4.2	1	30	Deionized water
Chemical cleaning (with or without US)	2.2	4.2	1	30	NaOH / Ultrasil
Second rinsing	2	4.2		5	Deionized water
Final water flux	2	3	1-3	90	Deionized water

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246 **Table 3: Experimental cleaning conditions: a) flat sheet membranes and b) tubular membranes.**

247 a)

Flat sheet membranes				
Test number	Feed stream	Cleaning agent	T (°C)	Concentration
1	Renylat 45	P3 Ultrasil 115	35	0.5% v/v
2	BSA	P3 Ultrasil 115	35	0.5% v/v
3	BSA	NaOH	35	pH 11
4	BSA/CaCl ₂	P3 Ultrasil 115	35	0.5% v/v

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*T:temperature

249 b)

Tubular membranes				
Test number	Feed stream	Cleaning agent	T (°C)	Concentration
5	Renylat 45	P3 Ultrasil 115	45	0.9% v/v
6	BSA	P3 Ultrasil 115	45	0.9% v/v
7	BSA	NaOH	45	pH 11
8	BSA/CaCl ₂	P3 Ultrasil 115	45	0.9% v/v

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*T:temperature

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253 2.4.3. Ultrasounds application

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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 25°C and pH 10 (test A) and at temperature of 35°C 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.

273 It is important to note that each test was carried out with and without US
274 application under the same experimental conditions in order to evaluate the effect of US
275 on the cleaning performance.

276 277 278 279 **2.4.4. Evaluation of the cleaning efficiency and US improvement**

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281
282 The criterion employed to assess the cleaning procedure was the evaluation of the
283 cleaning efficiency (CE). This parameter was calculated according Eq.4 defined by
284 [26]:

$$285 \quad CE (\%) = \frac{R_t - R_c}{R_t - R_m} \cdot 100 \quad (4)$$

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

$$290 \quad CE_{ENH} (\%) = \frac{CE_{withUS} - CE}{CE} \cdot 100 \quad (5)$$

291 292 293 294 295 **3. Results**

296 297 **3.1. Membrane fouling**

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299 Fig. 2 shows the flux reduction in the fouling tests. Values were calculated
300 dividing the final permeate flux by the initial flux measured using distilled water. It was
301 observed that Renylat 45 was the feed stream that caused the highest membrane fouling
302 (the highest flux decrease for all the membranes), followed by BSA/CaCl₂ solution and
303 finally by BSA solution. As previously reported by Shi et al. [12], the presence of
304 calcium in the feed solution increased membrane fouling since this cation can form a
305 bridge between proteins and membrane, as well as among proteins. In addition, the
306 heterogeneous composition of Renylat 45, with both salts and lactose, enhanced
307 membrane fouling [27].

309 In a previous study [18], it was reported that the **mean particle** size of the Renylat
 310 45 solution was 971.1 nm (much more higher than the other two fouling solutions). In
 311 this case, fouling solution size is an indicator of the particles aggregation degree. The
 312 heterogeneous composition of Renylat 45 leads to a higher **particle** size solution. Fig. 3
 313 shows the particle size distribution for this solution (sample was measured three times,
 314 **test 1, 2 and 3 as it can be observed in Fig. 3**). It can be observed that the peak with the
 315 highest intensity corresponds with the above mentioned particle size.

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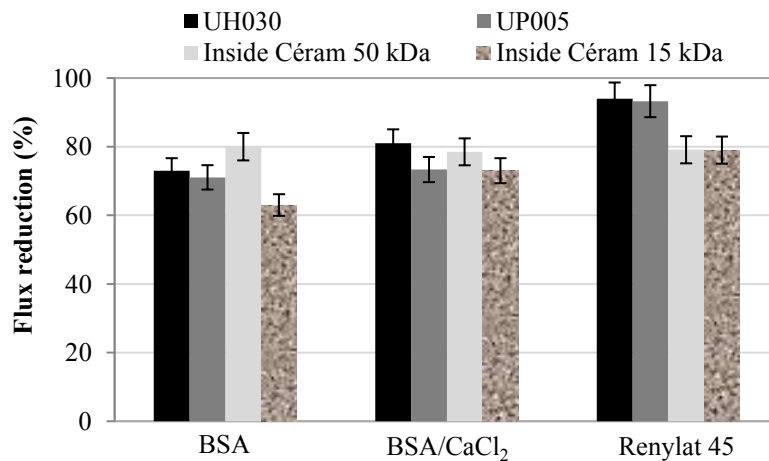
317 On the other hand, Renylat 45 caused higher fouling for organic than for inorganic
 318 membranes. In this way, Hofs et al. [28] reported that fouling degree is higher for
 319 organic than for inorganic membranes, at least when membranes were fouled with lake
 320 water. In addition, this group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

324

325 For BSA and BSA/CaCl₂ solutions, UH030 and Inside Céram 50 kDa were the
 326 membranes that presented the highest flux decrease. The main reason could be related
 327 with the molecular weight cut off of these membranes, since the pore size of both
 328 membranes are much closer to the BSA size (66 kDa). This was also observed by Qu et
 329 al. [29]. These authors fouled three PES membranes (with molecular weight cut-offs of
 330 10, 30 and 100 kDa) with extracellular polymeric substances.

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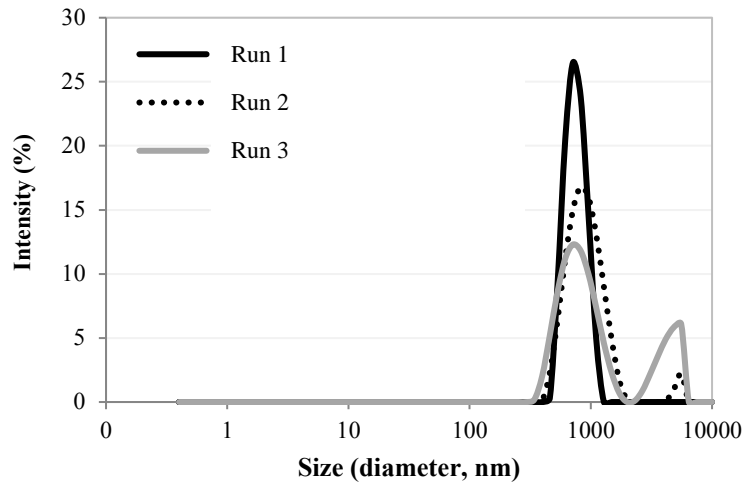
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Figure 2: Percentage flux reduction for all the membranes.

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Figure 3: Renylat 45 size distribution.

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345 3.2. US frequency selection.

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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].**

367

Table 4: CE_{ENH} in the tests for frequency selection.

Membrane	Test	20 kHz	25 kHz	30 kHz	38 kHz
UH030	A	7.3	14.9	5.4	9.1
	B	5.3	3.2	0	1.1
UP005	A	7.0	35.3	0	0
	B	12.7	0	0	0

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371 3.3. Effect of US applied to the cleaning solution on cleaning efficiency

372

373 Fig. 4 shows the CE values with and without applying US to the cleaning solution
 374 for the four membranes tested (UH030, UP005, Inside Céram 50 kDa and Inside Céram
 375 15 kDa). In general terms, US application improved the membrane cleaning since
 376 higher CE values with US than without US were achieved (at the same experimental
 377 conditions). The average CE_{ENH} for the eight tests using US and for each membrane
 378 were 3.8, 3.4, 3.4 and 6.1% for UH030, UP005, Inside Céram 50 kDa and Inside Céram
 379 15 kDa, respectively. It is important to remark that Inside Céram 15 kDa achieved the
 380 highest improvement in terms of CE with US application since the lowest CE values
 381 without US was measured. In this way, membrane Inside Céram 15 kDa obtained the
 382 lowest CE values, especially for tests 6 and 7. This fact could be related with the degree
 383 of reversible/irreversible resistance, since Inside Céram 15 kDa was the membrane that
 384 had the highest irreversible fouling (25.8%, 77.6%, 60.6% and 79.0% for membranes
 385 UH030, UP005, Inside Céram 50 kDa and Inside Céram 15 kDa, respectively), i.e., the
 386 flux recovery was the lowest after water rinsing.

387

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

396

397 The positive effect of the US on the membrane cleaning was mainly
 398 sonochemical. This was proved since no significant enhancement of the CE was
 399 obtained by applying US to distilled water in absence of NaOH (data not shown). In this
 400 way, US enhanced the hydrolysis of proteins at the pH of the cleaning solution.
 401 Denaturation of BSA may also be a mechanism enhanced by US for the detaching of
 402 adsorbed BSA from the membrane [31,32].

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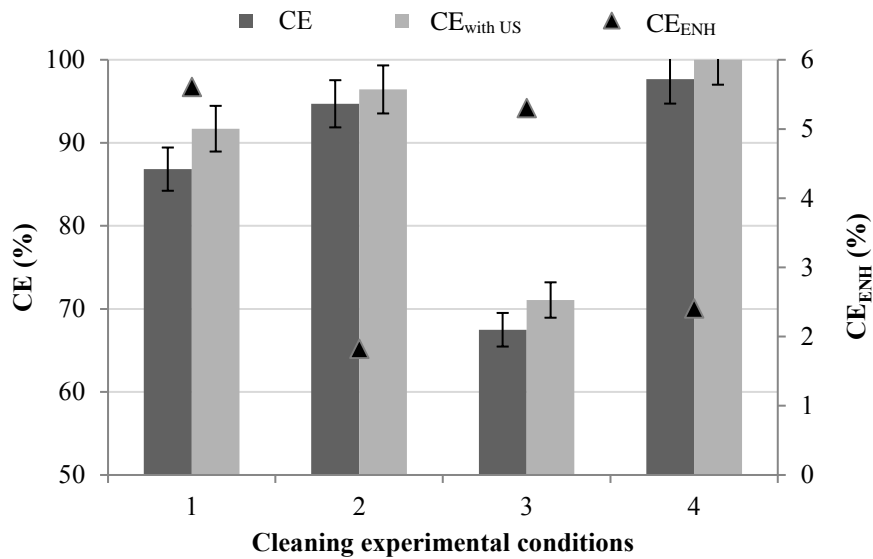
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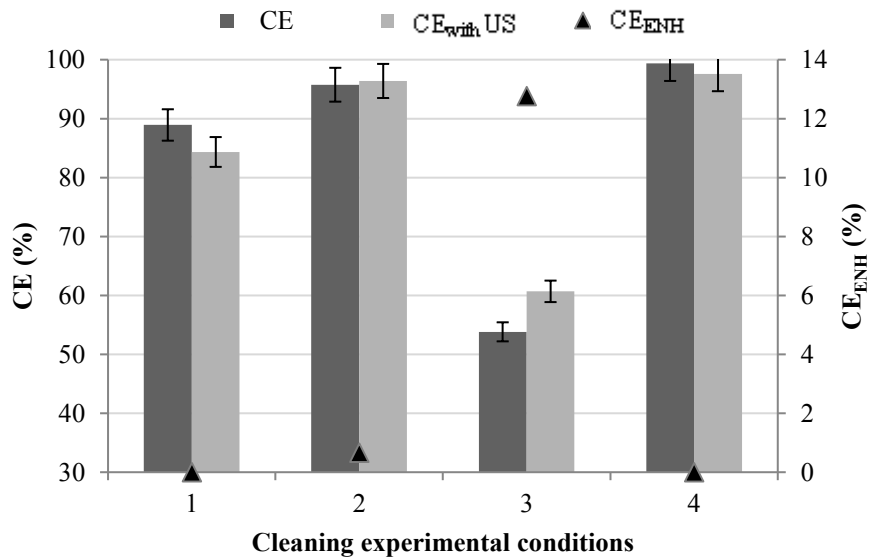
Similar results were obtained by Maskooki et al. [33], who applied US (after submerging the membrane module in a bath) for the cleaning of polyvinylidene fluoride UF membranes used in the dairy industry. The results demonstrated that US application with ethylenediaminetetraacetic acid at low concentrations (1-3 mM) was effective to clean the membranes and the reported improvement percentage with US was around 8%.



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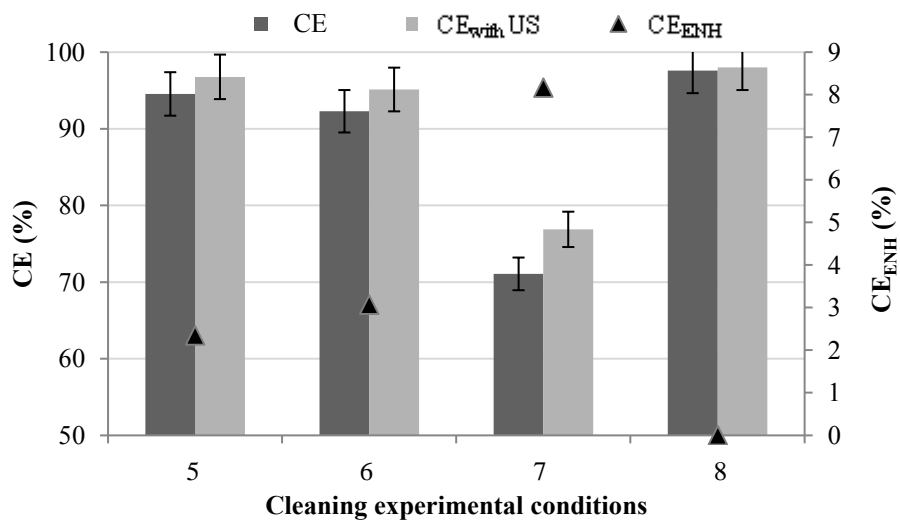
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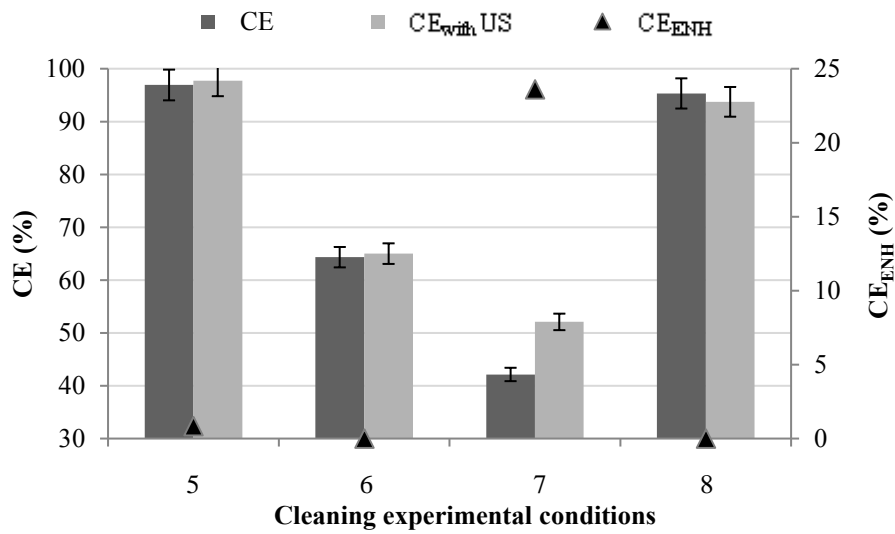
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Figure 4: Cleaning efficiency applying US to the cleaning solution and US improvement for: a) UH030, b) UP005, c) Inside Céram 50 kDa and d) Inside Céram 15 kDa.

436 **3.4. Effect of US submerging the membrane module**

437

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

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

459

460 **Table 5: CE_{ENH} for the different US application modes: a) Placing the membrane**
 461 **module at the bottom of the tank. b) Placing the membrane module at 3 cm of the bottom of the tank.**
 462 **c) applying US to the cleaning solution.**

463

a)

Test	Inside Céram 50 kDa	Inside Céram 15 kDa	UH030	UP005
1	5.7	0	15.2	12.5
2	6.8	50.7	3.8	0
3	30.4	74.3	0	0
4	1.1	0	2.4	0

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465

b)

Test	Inside Céram 50 kDa	Inside Céram 15 kDa	UH030	UP005
1	4.9	0.4	14.7	10.8
2	5.5	29.1	3.9	0
3	18.8	78.6	15.4	0
4	1.0	0	2.4	0.6

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468 c)

Test	Inside Céram 50 kDa	Inside Céram 15 kDa	UH030	UP005
1	2.4	0.8	5.6	0
2	3.1	0	1.8	0.7
3	8.2	23.1	5.3	12.8
4	0	0	2.4	0

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472 3.5. Comparison between the different US application modes.

473

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

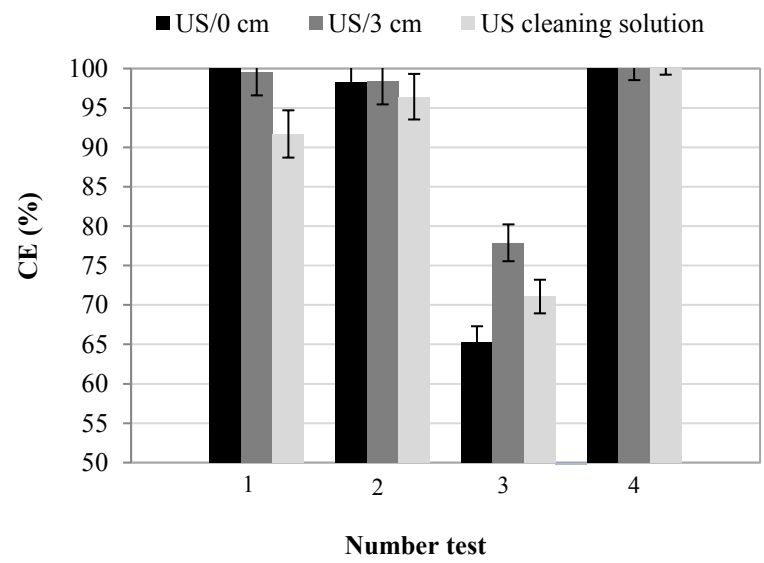
493

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

498

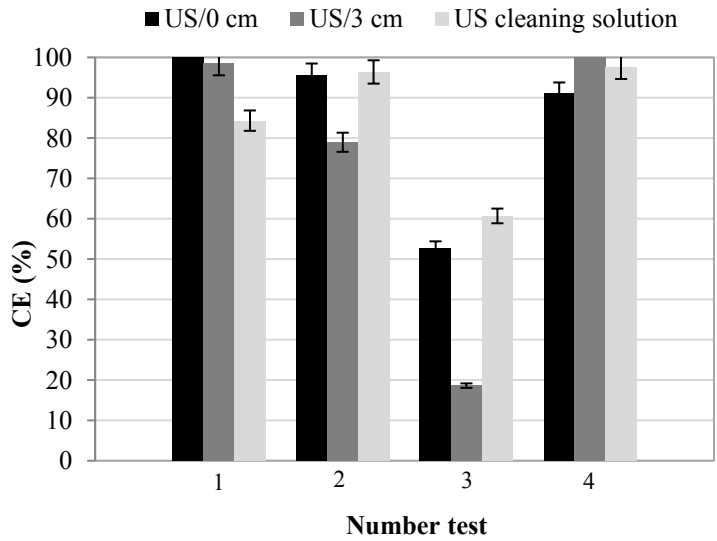
499 Kyllönen et al. [36] reported that when the membrane module is submerged inside
500 the US bath, there are energy losses due to the resistance that the membrane module
501 offers. Thus, for industrial applications it has to be assessed if the energy loss and the
502 disadvantage of submerging the modules makes up for the lower CE achieved when
503 cations concentration is high.

504 a)



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506 b)



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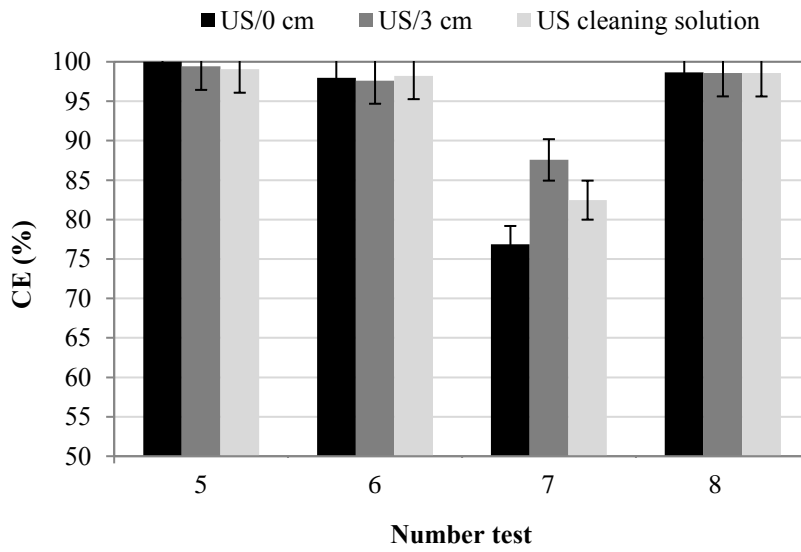
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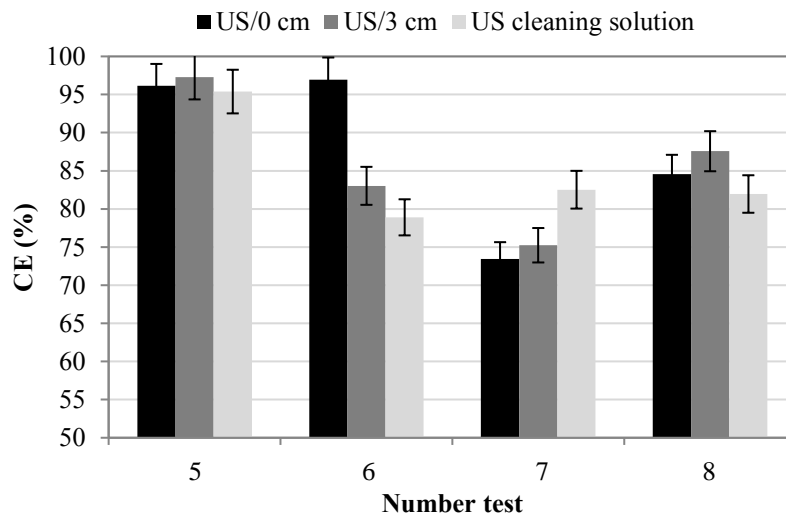
516 c)



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519 d)



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522 **Figure 5: CE comparing the different US application mode for: a) UH030,**
523 **b) UP005, c) Inside Céram 50 kDa and d) Inside Céram 15 kDa.**

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532 **4. Conclusions**

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

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

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

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

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558 **References**

559 [1] E. Alventosa-deLara, S. Barredo-Damas, M.I. Alcaina-Miranda, M.I. Iborra-
560 Clar, Study and optimization of the ultrasound-enhanced cleaning of an ultrafiltration
561 ceramic membrane through a combined experimental-statistical approach, *Ultrason.*
562 *Sonochem.* 21 (2014) 1222–1234.

563 [2] A. Saxena, B.P. Tripathi, M. Kumar, V.K. Shahi, Membrane-based techniques
564 for the separation and purification of proteins: an overview, *Adv. Colloid Interface Sci.*
565 145 (2009) 1–22.

566 [3] H. Zhu, M. Nyström, Cleaning results characterized by flux , streaming
567 potential and FTIR measurements, *Colloids Surfaces A Physicochem. Eng. Asp.* 138
568 (1998) 309–321.

- 569 [4] R.S. Juang, K.H. Lin, Flux recovery in the ultrafiltration of suspended
570 solutions with ultrasound, *J. Memb. Sci.* 243 (2004) 115–124.
- 571 [5] H. Kyllönen, P. Pirkonen, M. Nyström, J. Nuortila-Jokinen, A. Grönroos,
572 Experimental aspects of ultrasonically enhanced cross-flow membrane filtration of
573 industrial wastewater, *Ultrason. Sonochem.* 13 (2006) 295–302.
- 574 [6] S. Muthukumaran, S. Kentish, M. Ashokkumar, G. Stevens, Mechanisms for
575 the ultrasonic enhancement of dairy whey ultrafiltration, *J. Memb. Sci.* 258 (2005) 106–
576 114.
- 577 [7] S. Popović, M. Djurić, S. Milanović, M.N. Tekić, N. Lukić, Application of an
578 ultrasound field in chemical cleaning of ceramic tubular membrane fouled with whey
579 proteins, *J. Food Eng.* 101 (2010) 296–302.
- 580 [8] K. Chi-Chuan, D.A.D. Genuino, K.K.P. Rivera, M.D.G. De Luna, Ultrasonic
581 cleaning of polytetrafluoroethylene (PTFE) membrane fouled by natural organic matter
582 (NOM), *J. Memb. Sci.* 497 (2016) 450–457.
- 583 [9] S. Muthukumaran, S.E. Kentish, G.W. Stevens, M. Ashokkumar, R. Mawson,
584 The application of ultrasound to dairy ultrafiltration: The influence of operating
585 conditions, *J. Food Eng.* 81 (2007) 364–373.
- 586 [10] S. Muthukumaran, K. Yang, A. Seuren, S. Kentish, M. Ashokkumar, G.W.
587 Stevens, F. Grieser, The use of ultrasonic cleaning for ultrafiltration membranes in the
588 dairy industry, *Sep. Purif. Technol.* 39 (2004) 99–107.
- 589 [11] M.F.N. Secondes, V. Naddeo, V. Belgiorno, F. Ballesteros, Removal of
590 emerging contaminants by simultaneous application of membrane ultrafiltration,
591 activated carbon adsorption, and ultrasound irradiation, *J. Hazard. Mater.* 264 (2014)
592 342–349.
- 593 [12] X. Shi, G. Tal, N.P. Hankins, V. Gitis, Fouling and cleaning of ultrafiltration
594 membranes: A review, *J. Water Process Eng.* 1 (2014) 121–138.
- 595 [13] V. Naddeo, L. Borea, V. Belgiorno, Sonochemical control of fouling
596 formation in membrane ultrafiltration of wastewater: Effect of ultrasonic frequency, *J.*
597 *Water Process Eng.* 8 (2014) 92–97.
- 598 [14] S. Muthukumaran, S. Kentish, S. Lalchandani, M. Ashokkumar, R. Mawson,
599 G.W. Stevens, F. Grieser, The optimisation of ultrasonic cleaning procedures for dairy
600 fouled ultrafiltration membranes, *Ultrason. Sonochem.* 12 (2005) 29–35.
- 601 [15] J. Li, R.D. Sanderson, E.P. Jacobs, Ultrasonic cleaning of nylon
602 microfiltration membranes fouled by Kraft paper mill effluent, *J. Memb. Sci.* 205
603 (2002) 247–257.
- 604 [16] K.K. Latt, T. Kobayashi, Ultrasound-membrane hybrid processes for
605 enhancement of filtration properties., *Ultrason. Sonochem.* 13 (2006) 321–328.
- 606 [17] R. Naim, I. Levitsky, V. Gitis, Surfactant cleaning of UF membranes fouled
607 by proteins, *Sep. Purif. Technol.* 94 (2012) 39–43.
- 608 [18] M.J. Luján Facundo, *Influencia de la Aplicación de Ultrasonidos en la*
609 *Limpieza de Membranas de Ultrafiltración Empleadas en Separación de Proteínas en la*
610 *Industria Láctea*, Universitat Politècnica de València, 2016.
- 611 [19] N. Norazman, W. Wu, H. Li, V. Wasinger, H. Zhang, V. Chen, Evaluation of
612 chemical cleaning of UF membranes fouled with whey protein isolates via analysis of

613 residual protein components on membranes surface, *Sep. Purif. Technol.* 103 (2013)
614 241–250.

615 [20] C. Astudillo, J. Parra, S. González, B. Cancino, A new parameter for
616 membrane cleaning evaluation, *Sep. Purif. Technol.* 73 (2010) 286–293.

617 [21] M. Rabiller-Baudry, M. Le Maux, B. Chaufer, L. Begoin, Characterisation of
618 cleaned and fouled membrane by ATR—FTIR and EDX analysis coupled with SEM:
619 application to UF of skimmed milk with a PES membrane, *Desalination.* 146 (2002)
620 123–128.

621 [22] S.S. Popović, M.N. Tekić, M.S. Djurić, Kinetic models for alkali and
622 detergent cleaning of ceramic tubular membrane fouled with whey proteins, *J. Food*
623 *Eng.* 94 (2009) 307–315.

624 [23] T. Kobayashi, T. Kobayashi, Y. Hosaka, N. Fujii, Ultrasound-enhanced
625 membrane-cleaning processes applied water treatments: influence of sonic frequency on
626 filtration treatments, *Ultrasonics.* 41 (2003) 185–190.

627 [24] X. Li, J. Yu, A.G. Agwu Nnanna, Fouling mitigation for hollow-fiber UF
628 membrane by sonication, *Desalination.* 281 (2011) 23–29.

629 [25] M.O. Lamminem, H.W. Walker, L.K. Weavers, Mechanisms and factors
630 influencing the ultrasonic cleaning of particle-fouled ceramic membranes, *J. Memb. Sci.*
631 237 (2004) 213–223.

632 [26] P. Matzinos, R. Álvarez, Effect of ionic strength on rinsing and alkaline
633 cleaning of ultrafiltration inorganic membranes fouled with whey proteins, *J. Memb.*
634 *Sci.* 208 (2002) 23–30.

635 [27] U. Merin, M. Cheryan, Factors affecting the mechanism of flux decline
636 during ultrafiltration of cottage cheese whey, *J. Food Process. Preserv.* 4 (1980) 183–
637 198.

638 [28] B. Hofs, J. Ogier, D. Vries, E.F. Beerendonk, E.R. Cornelissen, Comparison
639 of ceramic and polymeric membrane permeability and fouling using surface water, *Sep.*
640 *Purif. Technol.* 79 (2011) 365–374.

641 [29] F. Qu, H. Liang, J. Zhou, J. Nan, S. Shao, J. Zhang, G. Li, Ultrafiltration
642 membrane fouling caused by extracellular organic matter (EOM) from *Microcystis*
643 *aeruginosa*: Effects of membrane pore size and surface hydrophobicity, *J. Memb. Sci.*
644 449 (2014) 58–66.

645 [30] M. Cai, S. Wang, Y. Zheng, H. Liang, Effects of ultrasound on ultrafiltration
646 of *Radix astragalus* extract and cleaning of fouled membrane, *Sep. Purif. Technol.* 68
647 (2009) 351–356.

648 [31] L. Paugam, D. Delaunay, N.W. Diagne, M. Rabiller-Baudry, Cleaning of
649 skim milk PES ultrafiltration membrane: On the real effect of nitric acid step, *J. Memb.*
650 *Sci.* 428 (2013) 275–280.

651 [32] A. Maskooki, S.A. Mortazavi, A. Maskooki, Cleaning of spiralwound
652 ultrafiltration membranes using ultrasound and alkaline solution of EDTA,
653 *Desalination.* 264 (2010) 63–69.

654 [33] A. Maskooki, T. Kobayashi, S.A. Mortazavi, A. Maskooki, Effect of low
655 frequencies and mixed wave of ultrasound and EDTA on flux recovery and cleaning of
656 microfiltration membranes, *Sep. Purif. Technol.* 59 (2008) 67–73.

657 [34] D. Chen, L.K. Weavers, H.W. Walker, Ultrasonic control of ceramic
658 membrane fouling by particles: effect of ultrasonic factors., *Ultrason. Sonochem.* 13
659 (2006) 379–387.

660 [35] D. Chen, L. Weavers, H. Walker, J. Lenhart, Ultrasonic control of ceramic
661 membrane fouling caused by natural organic matter and silica particles, *J. Memb. Sci.*
662 276 (2006) 135–144.

663 [36] H.M. Kyllönen, P. Pirkonen, M. Nyström, Membrane filtration enhanced by
664 ultrasound: a review, *Desalination.* 181 (2005) 319–335.

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