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1 **TREATMENT OF TABLE OLIVE PROCESSING WASTEWATERS**
2 **USING NOVEL PHOTOMODIFIED ULTRAFILTRATION**
3 **MEMBRANES AS FIRST STEP FOR RECOVERING PHENOLIC**
4 **COMPOUNDS**

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16

17 **ABSTRACT**

18 Table olive processing wastewaters (TOPW) cause many environmental problems due
19 to their high salt concentration and total phenolic content (TPC). In order to reduce the
20 environmental impacts and get economic benefits by recovering by-products,
21 ultrafiltration (UF) was applied for treating TOPW. However, UF membranes have
22 serious problems caused by fouling, which can be overcome using membrane
23 modification techniques. Surface modification via UV irradiation in the presence of two
24 hydrophilic compounds (polyethylene glycol, PEG, and aluminium oxide, Al₂O₃) was
25 performed to obtain membranes with high reductions of colour and chemical oxygen
26 demand (COD) and to keep the TPC as high as possible. Commercial polyethersulfone

27 (PES) membranes with a cut-off of 30 kDa were used. Effectiveness of surface
28 modification was evaluated using FTIR-ATR spectroscopy and membrane performance
29 was studied by calculating the rejection ratios of colour, COD and TPC. Results
30 demonstrated that UF is a useful pre-treatment for TOPW in which a permeate stream
31 rich in TPC can be obtained. Important reductions of colour and COD were also
32 observed. Membranes photomodified with Al₂O₃ displayed superior antifouling
33 properties and desirable rejection values, keeping high the TPC (> 95 %). Therefore, UF
34 using modified membranes is an appropriate and sustainable technique for treating
35 TOPW.

36

37 **KEYWORDS** hydrophilicity; phenolic compound; table olive processing wastewater;
38 antifouling; surface modification.

39

40 **1. INTRODUCTION**

41 Phenolic compounds are the most abundant antioxidants in the Mediterranean diet and
42 they play a crucial role in human health and nutrition due to their behaviour as
43 preventative agents against several diseases and oxidative stress [1]. As a natural
44 resource to obtain phenolic compounds, the olive fruit and the study of traditional
45 industrial processes used for producing olive oil as well as for preparing table olives are
46 acquiring more and more importance over the years, principally in studies developed in
47 Mediterranean countries (such as Spain, Tunisia, Turkey, Italy and Greece). Some
48 researchers focused their studies on the psychological and physiological benefits of the
49 phenolic compounds due to their important biological properties (such as antioxidant,
50 antimutagenic, anticarcinogenic and antiglycemic properties) [2-4], whereas other

51 researchers tried to remove partially or completely to obtain a palatable final product
52 because phenolic compounds can be embittering [5,6].

53

54 In our case, we study the residual brines from table olive processing or table olive
55 processing wastewaters (TOPW). These wastewaters consist of high salt concentrations
56 (sodium chloride and sodium hydroxide), phenolic compounds (which affects some
57 properties of the final marketable product such as taste, colour and texture [7]), sugars,
58 acids, tannins, pectins, carotenoids, oil residues and trace amounts of various metals.
59 Due to their high organic content and high concentrations of salt and phenolic
60 compounds, these wastewaters show antimicrobial, exotoxic and phytotoxic properties
61 [8,9]. During their discharge to water, TOPW heavily pollute the urban wastewaters,
62 streams and rivers to which they join. Therefore, the treatment of this type of
63 wastewater makes them into an important environmental concern. Among all the
64 aforementioned compounds present in TOPW, phenolic compounds are powerful
65 organic pollutants and their presence in the environment must be controlled. Thus, it
66 would be very interesting to remove them from these wastewaters to obtain high-value
67 products, especially hydroxytyrosol and tyrosol, which have a high antioxidant activity
68 [1].

69

70 Several technologies based on biological, chemical oxidation and separation processes
71 have been used for treating TOPW by different research groups. Chatzisyneon *et al.*
72 applied heterogeneous photocatalytic treatments to an effluent from TOPW by which
73 they obtained good efficiencies in decolourisation (> 90 %) and phenols [9]. Katsoni *et*
74 *al.* used wet-air oxidation process for treating TOPWs, obtaining more than 90 % of
75 phenol degradation and decolourisation [10]. El-Abbassi *et al.* studied the application of

76 ultrafiltration process on both olive mill wastewaters and TOPWs and they
77 demonstrated that such process can be efficient in recovering phenolic compounds (~ 40
78 %), mainly in acidic wastewaters [11].

79

80 This paper deals with the study of the effect and performance of different modified
81 ultrafiltration membranes that might be used to obtain a stream rich in phenolic
82 compounds from TOPW and a stream poor in these compounds with less
83 dangerousness. The aims of this work were to separate organic compounds of high
84 molecular weight from TOPW with high total phenolic content (TPC) using UF process
85 as clean technology (with easy and rapid operation) due to the high added value of
86 phenolic compounds in other industries (such as cosmetics, pharmaceuticals and
87 chemical processing among others); and to reduce the fouling suffered by these
88 ultrafiltration membranes and the volume and dangerousness of TOPW generated. The
89 membranes used were modified by ultraviolet (UV) irradiating their surface in the
90 presence of two additives from different nature: polyethylene glycol (PEG) of 400 Da
91 and aluminium oxide (Al_2O_3). The influence of both additives on membrane
92 performance was investigated. The performance of all membranes was evaluated in
93 terms of the presence of TPC in the permeate stream, chemical oxygen demand (COD)
94 removal, decolourisation and fouling/rinsing experiments.

95

96 **2. EXPERIMENTAL**

97 *2.1. TOPW samples*

98 Table olive processing wastewater (TOPW) samples were donated by Depuración de
99 Aguas del Mediterráneo (DAM), located in the region of Valencia (Spain). The samples
100 were freshly used for physicochemical determinations and UF experiments.

101

102 *2.2. Chemicals*

103 Nano-sized Al₂O₃ (primary size of 13 nm) and PEG (400 Da) were used as additives
104 during surface modification and both chemicals were supplied by Sigma Aldrich
105 (Spain). Folin-Ciocalteu reagent was purchased from Merck (Spain) and sodium
106 carbonate was supplied by Panreac (Spain). Tyrosol was used as standard to determine
107 the total phenolic content and was also purchased from Sigma-Aldrich (Spain).
108 Deionised water was used throughout this study.

109

110 *2.3. Membrane*

111 Commercial flat-sheet membranes made of polyethersulfone (PES) with a nominal
112 molecular weight cut-off of 30 kDa (Synder Filtration, USA) were used for membrane
113 modification. Their effective surface area was 100 cm². As it was proposed by Susanto
114 and Ulbricht [12], commercial membranes were chosen to minimize the inconsistency
115 in membrane properties.

116

117 *2.4. Surface modification*

118 An UV illumination system equipped with two UV mercury lamps provided
119 homogeneous illumination of up to 100 cm² with an intensity of approximately 30
120 mW/cm². The employed modification equipment was described elsewhere [13].
121 Commercial membranes were dipped in different concentrations of grafting solutions
122 (aqueous solutions with PEG dissolved and Al₂O₃ nanoparticles well-dispersed) for 5
123 min and then were UV irradiated under atmosphere with controlled relative humidity for
124 10 min. Thereafter, the modified membranes were extensively rinsed with tap water to
125 remove the non-reacted compounds and were sequentially washed with deionised water

126 at room temperature for 30 min, at $50 \pm 2^\circ\text{C}$ for 2h and finally again at room
127 temperature for 30 min.

128

129 *2.5. Fourier transform IR spectroscopy with attenuated total reflectance (FTIR-*
130 *ATR) analysis*

131 The chemical structure of the different modified membranes was confirmed by the
132 FTIR-ATR spectroscopic technique. FTIR-ATR spectra were recorded on a Thermo
133 Nicolet[®] Nexus spectrometer. The ATR accessory contained a ZnSe crystal at a nominal
134 incident angle of 45° . For each measurement, 128 scans were performed for an
135 operating range from 600 to 4000 cm^{-1} with a resolution of 8 cm^{-1} . Also, this technique
136 may be used for qualitative detection of foulants on the membrane surface [14].

137

138 *2.6. Psychochemical characterization of TOPW samples by colorimetric*
139 *analyses*

140 Colorimetric reactions are widely used to characterize wastewater samples by the UV-
141 VIS spectrophotometer method, which is rapid, low-cost and applicable at laboratory
142 scale [15]. Chemical oxygen demand (COD) was measured using a colorimetric method
143 recommended by the manufacturer Hach Lange (Germany). Many TOPW contain
144 chloride concentrations far greater than $15\text{ g Cl}^-/\text{L}$. In these cases, samples of TOPW
145 should be diluted up to a concentration value of $1.5\text{ g Cl}^-/\text{L}$ (the highest concentration
146 value of Cl^- recommended by the manufacturer) with ultrapure water to avoid any
147 possible interference in the results obtained. Cl^- concentration was measured by using
148 kit Hach Lange LCK 311. 2 mL of sample was added to Hach reflux tubes and mixed
149 properly (using kits LCK 114 and 314). The mixtures were then refluxed in a Hach
150 Lange COD reflux reactor at 150°C for 2 h. After cooling at 20°C , samples were

151 analysed on a Hach-Lange DR 6000 UV-VIS spectrophotometer. On such equipment,
152 the colour of TOPW was determined by the difference of absorbances at 440 and 700
153 nm ($A_{440}-A_{700}$) [1].

154

155 Total phenolic content (TPC) was evaluated colorimetrically by the Folin-Ciocalteu
156 method [16], presenting its results as tyrosol equivalents (mg of tyrosol equivalents per
157 liter of TOPW).

158

159 All physicochemical analyses were carried out at least in triplicate.

160

161 2.7. Ultrafiltration

162 UF experiments were carried out at 25 °C in a standard ultrafiltration system (VF-S11
163 UF plant, Orelis, France) with 10 L in volume, which was described elsewhere [17]. All
164 the experiments were performed in total recirculation mode, except during the rinsing
165 step. Each PES membrane was initially compacted with deionised water for 30 min at
166 200 kPa and constant cross-flow velocity (2.08 m/s), recording the pure water flux J_0
167 ($L/m^2 \cdot h$) at the end of the compaction test. After that, a cycle consisting of two different
168 steps was carried out for each membrane: a TOPW ultrafiltration at 200 kPa for 2h
169 where the permeate flux J_f ($L/m^2 \cdot h$) was measured, and a rinsing process with deionised
170 water for 30 min in which the water flux J_w ($L/m^2 \cdot h$) was recorded again. Both fluxes
171 were measured by gravimetric method. To investigate the fouling-resistant capability of
172 each membrane, fouling degree (FD) and flux recovery ratio (FRR) were calculated by:

$$173 \quad FD(\%) = \left(\frac{J_{f1} - J_{f2}}{J_{f1}} \right) \cdot 100 \quad \text{Eq. (1)}$$

174
$$FRR(\%) = \left(\frac{J_W}{J_0} \right) \cdot 100 \quad \text{Eq. (2)}$$

175 where J_{f1} is the permeate flux obtained at the beginning of the fouling process, J_{f2} is the
 176 permeate flux of the membranes at the end of the fouling process (2 h).

177

178 To evaluate the membrane separation efficiency for rejection of phenolic compounds
 179 from the feed solution, the following expression was used:

180
$$R_{TPC}(\%) = \left(1 - \frac{C_p}{C_f} \right) \cdot 100 \quad \text{Eq. (3)}$$

181 where R_{TPC} is the rejection rate of total phenolic compounds, C_p is the permeate
 182 concentration of phenolic compounds and C_f is the feed concentration of phenolic
 183 compounds.

184

185 In the same way, decolourisation and COD removal were determined as follows:

186
$$DC(\%) = \left(1 - \frac{OD_p}{OD_f} \right) \cdot 100 \quad \text{Eq. (4)}$$

187
$$R_{COD}(\%) = \left(1 - \frac{COD_p}{COD_f} \right) \cdot 100 \quad \text{Eq. (5)}$$

188 where DC is the decolourisation rate, OD_p is the permeate optical density, OD_f is the
 189 feed optical density, R_{COD} is the rejection rate of COD, COD_p and COD_f are the
 190 permeate concentration and the feed concentration of COD, respectively.

191

192 **3. RESULTS AND DISCUSSION**

193 *3.1. TOPW samples characterization*

194 The physicochemical characteristics of TOPW samples are summarized in Table 1. This
195 effluent is acid, rich in salt concentration (high electrical conductivity) with a moderate
196 COD and dry matter compared with the wastewater used by other researchers [18]. As
197 phenolic compounds are considered as one of the most important pollutants, the amount
198 of phenolic compounds makes this type of wastewater even more toxic. In addition, Cl⁻
199 concentration indicates that TOPW samples must be diluted 30 times to obtain the COD
200 values, as is explained in Section 2.6.

201

202 *3.2. Membrane modification*

203 Table 2 presents the composition and characteristics for control PES membrane and all
204 the modified membranes with different additives concentration, where water contact
205 angle was measured by sessile drop method [19] and pore size was calculated using
206 Guerout-Elford-Ferry equation as it was reported by Wu *et al.* [20]. To observe if the
207 modification process was successfully achieved, it would be very important to
208 corroborate the presence of Al₂O₃ nanoparticles and PEG chains on the structure of the
209 membrane surface. Therefore, FTIR-ATR analyses were performed to characterize the
210 chemical structures of all the membranes tested and to identify the main foulants on
211 their membrane surface. TOPW chemical composition depends on the cultivar, soil
212 nature, climate, olives ripeness and table olive preparation process [11].

213

214 Fig. 1 shows the effect of fouling on the different membranes tested, where clean
215 membranes are represented by dotted line and fouled membranes are represented by a
216 solid line. Firstly, the success of the modification process can be observed in different
217 new absorption peaks appeared in the FTIR-ATR spectra of each modified membrane in
218 comparison with those obtained for the control membrane, which are displayed in Fig.

219 1(a). In this way, a new absorption band related to the UV irradiation of PES material
220 appeared at 1645 cm^{-1} , which could be assigned to the carboxyl group in asymmetric
221 stretching [21]. The presence of Al_2O_3 on the membrane surface is evidenced by three
222 small absorption peaks detected at approximately 620 , 795 and 1072 cm^{-1} (see Fig.
223 1(b)), which can be identified with different stretching vibrations and bending modes of
224 Al-O-Al bonds [22]. This last absorption peak coincides with the band related to the
225 ether group in PEG (should appear at 1080 cm^{-1}), which is commonly used to identify
226 the presence of this compound on membrane surfaces [23]. So, the analytical peak at
227 1072 cm^{-1} in modified membranes could be assigned to the sum of the presence of ether
228 group and the symmetric bending mode of Al-O-Al bond contributions (see Fig. 1(c)).
229 In the same way, an increasing intensity of the absorption band at $3300\text{-}3400\text{ cm}^{-1}$ could
230 be related to the incorporation of hydrated Al_2O_3 and hydroxyl groups from grafted
231 PEG chains on the membrane surface [24,25].

232

233 Secondly, FTIR-ATR spectra of clean membranes were compared in pairs to the spectra
234 of the fouled membranes, as is also shown in Fig. 1. The absorption band at $3300\text{-}3400$
235 cm^{-1} increased its intensity after fouling in all the membranes tested. This effect may be
236 due to OH groups of phenolic compounds, alcohols and carboxylic groups and also the
237 hydrogen vibration of amide N-H groups from olive wastewater samples [26]. As
238 Susanto *et al.* indicated, phenolic compounds basically consisted of aliphatic and
239 aromatic fraction having a significant absorption peak at $\sim 3400\text{ cm}^{-1}$ (phenol character)
240 [27]. A small band can be barely observed at $\sim 2900\text{-}2920\text{ cm}^{-1}$, which could be
241 associated to a possible overlap between two absorption peaks related to the asymmetric
242 (2925 cm^{-1}) and symmetric (2854 cm^{-1}) C-H stretching in aliphatic structures, such as
243 fatty acids and other long-chain structures [28]. A strong band appeared at 1650 cm^{-1} for

244 MK0 and increased in MK1 and MK2 at 1641 cm^{-1} , which is characteristic of aromatic
245 C=C vibrations, C=O stretching vibrations of amide groups (amide I), quinines and/or
246 conjugated ketones [27,29,30]. A slightly increased in intensity was observed at ~ 1520
247 cm^{-1} that could be assigned to the C=C stretching in aromatics as well as the N-H
248 deformation and C=N stretching (amide II) [28,31]. Also, a shoulder around 1200 cm^{-1}
249 could be identified with C-O stretching of aryl ethers and phenols [27,31]. Finally, an
250 absorption peak appeared at $948\text{-}950\text{ cm}^{-1}$ could be assigned to the vibrations of
251 polysaccharide-like substances [27,28].

252

253 3.3. Ultrafiltration

254 UF experiments were performed to investigate the efficiency of the separation process
255 for reducing colour and COD and at the same time for obtaining the highest content of
256 phenolic compounds (the lowest R_{TPC} possible) in the permeate stream. In the same
257 way, performances of the three different membranes (one control membrane and two
258 membranes modified via surface UV photografting) were compared among them.

259

260 Fig. 2 shows the evolution of the fouling degree (FD) during the UF treatment of
261 TOPW samples at a transmembrane pressure (ΔP) of 200 kPa, a crossflow velocity of
262 1.39 m/s and $25\text{ }^{\circ}\text{C}$ for 2 h. As it can be seen, the FD value of the control membrane
263 (MK0) increased rapidly within the first 20 min and continued to increase until to reach
264 a value of around 45 %. This increase is intimately related to the concentration
265 polarization and fouling phenomenon [32]. However, both modified membranes
266 exhibited an increase in their FD up to values of around 37-39 %, where MK1
267 (membrane modified with 0.5 wt% Al_2O_3) presented lower values than MK2
268 (membrane modified with 2 wt% PEG and 0.5 wt% Al_2O_3) at first 40 min and since

269 then, MK2 showed higher resistance to fouling. These behaviours could be due to the
270 presence of hydrophilic compounds on their surface structure. The most suitable
271 polymers used in membrane preparation for UF applications are materials with
272 hydrophobic character (polyvinylidene fluoride or PVDF, PES and PS), which are
273 susceptible to fouling phenomenon (either through adsorption or deposition of the
274 retained organic compounds). Several authors have demonstrated that the incorporation
275 of hydrophilic particles (organic, inorganic or a mixture of both natures) on the
276 membrane via surface modification improves the material hydrophilicity, which leads to
277 a successful reduction of the fouling phenomenon [33,34]. This statement is further
278 supported by the water contact angle values given in Table 2, where lower values of this
279 parameter indicate higher hydrophilic character of the material studied [19,35]. In this
280 way, the incorporation of PEG and Al₂O₃ nanoparticles (both are hydrophilic
281 compounds) on the membrane surfaces led to an increase in their hydrophilicity and
282 then, membranes presented higher resistance to fouling.

283

284 The evolution of the parameter flux recovery ratio (*FRR*) of each membrane obtained in
285 the UF treatment of TOPW samples is presented in Fig. 3. Rinsing process was
286 performed at a crossflow velocity of 2.08 m/s, 200 kPa and 25 °C during 30 min. After
287 that, the control membrane (MK0) showed a *FRR* value of about 41 %, which was the
288 lowest value among all membranes. This could be attributed to the severe fouling
289 produced by the adsorption of organic matter from TOPW onto the membrane material
290 (PES) [36]. As it can be observed in Fig. 3, both modified membranes presented high
291 *FRR* values in comparison with those obtained for MK0. These results indicated that the
292 hydrophobic interactions between the membrane surface and organic matter were
293 diminished, which can be removed by rinsing [37]. Therefore, the antifouling properties

294 of the commercial membranes were further enhanced after the incorporation of PEG and
295 Al_2O_3 on surface structure.

296

297 *3.3.1 Decolourisation (DC) of TOPW*

298 The pollutant power of TOPW is indicated by the dark colour of the samples. UF
299 treatment allows the rejection of a great part of organic matter and pigments, which
300 contribute to the colour of TOPW [11]. As it is shown in Fig. 4 (dark grey bars), dark
301 colour was reduced up to the range of 76-84.1 %, where the lowest DC value was
302 presented by MK0 (~ 76 % of TOPW colour). Hence, both modified membranes
303 showed higher reduction of DC than MK0 (~ 82-84 % of TOPW colour). This effect
304 could be due to the hydrophilicity of the grafted additives, that is, the higher affinity of
305 both additives (Al_2O_3 and PEG) for water than the PES material [13].

306

307 In addition, other researchers demonstrated that the highest *DC* value of TOPW samples
308 can be achieved at feed pH value between 4 and 5 (in our case, pH value is 4.75, see
309 Table 1), which may be related to the changes in turbidity and granulometry occurred at
310 these pH values [11].

311

312 *3.3.2 Removal of COD*

313 Results of COD removal for the different membranes tested are also displayed in Fig. 4.
314 As it can be seen (grey bars), MK0 and MK2 obtained COD removal efficiencies of
315 about 35-45 %, which are in accordance with those obtained by El-Abbassi *et al.* using
316 TOPW samples at similar feed pH [11]. However, MK1 presented the highest removal
317 value (~ 66 %) whereas MK2 had a lower removal value (~ 45 %), which demonstrates
318 the importance of the different nature of additives grafted on the membrane surface. The

319 inorganic nature of Al₂O₃ nanoparticles and its low water solubility reduced the existing
320 interactions between solute (organic matter) and the membrane surface due to its high
321 surface energy and then, its hydrophilic nature [38,39].

322

323 As other researchers demonstrated, improvement in COD removal is also related to the
324 surface modification process, in which pore size of the modified membranes decreased
325 in comparison with MK0 using photografting techniques [21,40].

326

327 *3.3.3 Recovery of total phenolic compounds (TPC)*

328 Fig. 4 summarizes rejection values obtained for total phenolic compounds (R_{TPC}) during
329 the UF of TOPW (light grey bars). All membranes showed moderate rejection of total
330 phenolic compounds except MK1 (membrane modified with Al₂O₃ nanoparticles),
331 which presented a reduction of phenolic compounds in TOPW lower than 10 %. These
332 results indicate that phenolic compounds were successfully recovered in the permeate
333 stream using the membrane MK1. This behaviour can be explained by the use of tyrosol
334 concentration as yardstick for measuring TPC. As Quiles *et al.* and Bulotta *et al.*
335 indicated, both hydroxytyrosol and tyrosol can be classified as phenolic alcohols, which
336 is a type of hydrophilic phenol [41,42]. The presence of Al₂O₃ nanoparticles on the
337 membrane surface reduced the interactions between organic compounds and surface
338 material (due to the higher affinity of Al₂O₃ for water than PES material [19,38]. This
339 fact facilitated the pass of compounds with high hydrophilicity through the membrane,
340 increasing the rejection of hydrophobic organic matter (which can be observed in the
341 results obtained for COD removal).

342

343 Membranes modified with the combination of PEG/Al₂O₃ presented high retention due
344 to the presence of PEG chains on their surface structure. Previous studies about PEG
345 and phenolic compounds in salt solutions at similar pH demonstrated that aromatic
346 molecules (such as phenolic compounds) tend to concentrate on the PEG-rich surface,
347 which may be related to the hydrogen bond interactions between the PEG chains and
348 the phenolic compounds [43]. However, this effect counteracts the behaviour of Al₂O₃
349 nanoparticles on the surface structure.

350

351 **4. CONCLUSIONS**

352 UF process is a useful tool for reducing colour (~ 76-85 %) and organic load (~ 36-66
353 % of COD removal) from table olive processing wastewaters. Therefore, it would be
354 very interesting to apply this process as a clean technology in pre-treatments of table
355 olive processing wastewaters due to its yields. Surface modification process of UF
356 membranes via UV irradiation in the presence of two hydrophilic compounds with
357 different nature (PEG and Al₂O₃) is a well-known technique to enhance the fouling-
358 resistant capability of the membrane surface and also, it can be successfully applied to
359 obtain selective membranes for the purpose of recovering important by-products as
360 phenolic compounds from the pretreated effluents. The success of the modification
361 process was analysed by FTIR-ATR spectroscopy and water contact angle
362 measurements. The effect of PEG and Al₂O₃ on the performance during UF experiments
363 was elucidated. Membranes photomodified with 0.5 wt% Al₂O₃ displayed superior
364 antifouling properties and desirable rejection values (~ 84 % of decolourisation and ~ 66
365 % of COD removal), keeping TPC as high as possible (> 95 %).

366

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372

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505

506 **7. LIST OF SYMBOLS**

507 **Variables**

- 508 A_{440} Absorbance at 440 nm (dimensionless)
- 509 A_{700} Absorbance at 700 nm (dimensionless)
- 510 C_f Concentration of phenolic compounds in the feed stream (mg of
 511 tyrosol/L)
- 512 COD_f Concentration of COD in the feed stream (g of O₂/L)
- 513 COD_p Concentration of COD in the permeate stream (g of O₂/L)

514	C_p	Concentration of phenolic compounds in permeate the stream (mg of
515		tyrosol/L)
516	DC	Decolourisation rate (%)
517	FD	Fouling degree (%)
518	FRR	Flux recovery ratio (%)
519	J_0	Pure water flux at the end of the compaction test ($L/m^2 \cdot h$)
520	J_f	Permeate flux during wastewater ultrafiltration ($L/m^2 \cdot h$)
521	J_{f1}	Permeate flux obtained at the beginning of the wastewater ultrafiltration
522		($L/m^2 \cdot h$)
523	J_{f2}	Permeate flux of the membranes at the end of the wastewater
524		ultrafiltration ($L/m^2 \cdot h$)
525	J_w	Permeate water flux during rinsing process ($L/m^2 \cdot h$)
526	OD_f	Feed optical density (dimensionless)
527	OD_p	Permeate optical density (dimensionless)
528	R_{COD}	Rejection rate of chemical oxygen demand (%)
529	R_{TPC}	Rejection rate of total phenolic compounds (%)
530	t	Operating time (h)
531	T	Operating temperature ($^{\circ}C$)
532	W_w	Weight of wet membranes (g)
533	ΔP	Transmembrane pressure (MPa)

534

535 **Abbreviations**

536	ATR	Attenuated total reflectance
537	COD	Chemical oxygen demand
538	DAM	Depuración de Aguas del Mediterráneo

539	FTIR-ATR	Fourier transform IR spectroscopy with attenuated total reflectance
540	PEG	Polyethylene glycol
541	PES	Polyethersulfone
542	PS	Polysulfone
543	PVDF	Polyvinylidene fluoride
544	TOPW	Table olive processing wastewater
545	TPC	Total phenolic content
546	UF	Ultrafiltration
547	UV	Ultraviolet
548	UV-VIS	Ultraviolet-visible

Table 1. Physicochemical characteristics of TOPW samples used.

Parameters	Mean value
pH	4.75±0.10
Electrical conductivity (mS/cm)	80.7±2.0
Turbidity (NTU)	427.8±4.0
Colour	0.38±0.5
COD (g of O ₂ /L)	7.25±0.26
Cl ⁻ (g/L)	41.12±1.94
Dry matter (g/L)	2.66±0.16
Total phenolic compounds (mg of tyrosol/L)	591.1±2.0

Table 2. Main characteristics and composition of the control membrane (MK0) and all the modified membranes (MK1 and MK2).

Membrane	Additive composition (wt%)		Water contact angle (°) ^a	Pore size (nm) ^b
	Al ₂ O ₃	PEG		
MK0	---	---	77.4±1.0	14.3±0.5
MK1	0.5	---	66.3±1.2	11.7±1.3
MK2	0.5	2.0	62.4±1.4	13.1±0.4

^a measured by sessile-drop method.

^b determined by water filtration method under constant transmembrane pressure (300 kPa) and calculated using Guerout-Elford-Ferry equation, in which pore size is related to membrane porosity and thickness, water flow through the membrane and water viscosity at 20 °C.

Table 3. Analysis of flux decline and fouling phenomenon for TOPW ultrafiltration.

Membrane	RFR (%)	Reversible fouling (%)	Irreversible fouling (%)
MK0	19.4	24.1	56.5
MK1	24.5	28.9	46.6
MK2	20.8	27.8	51.4

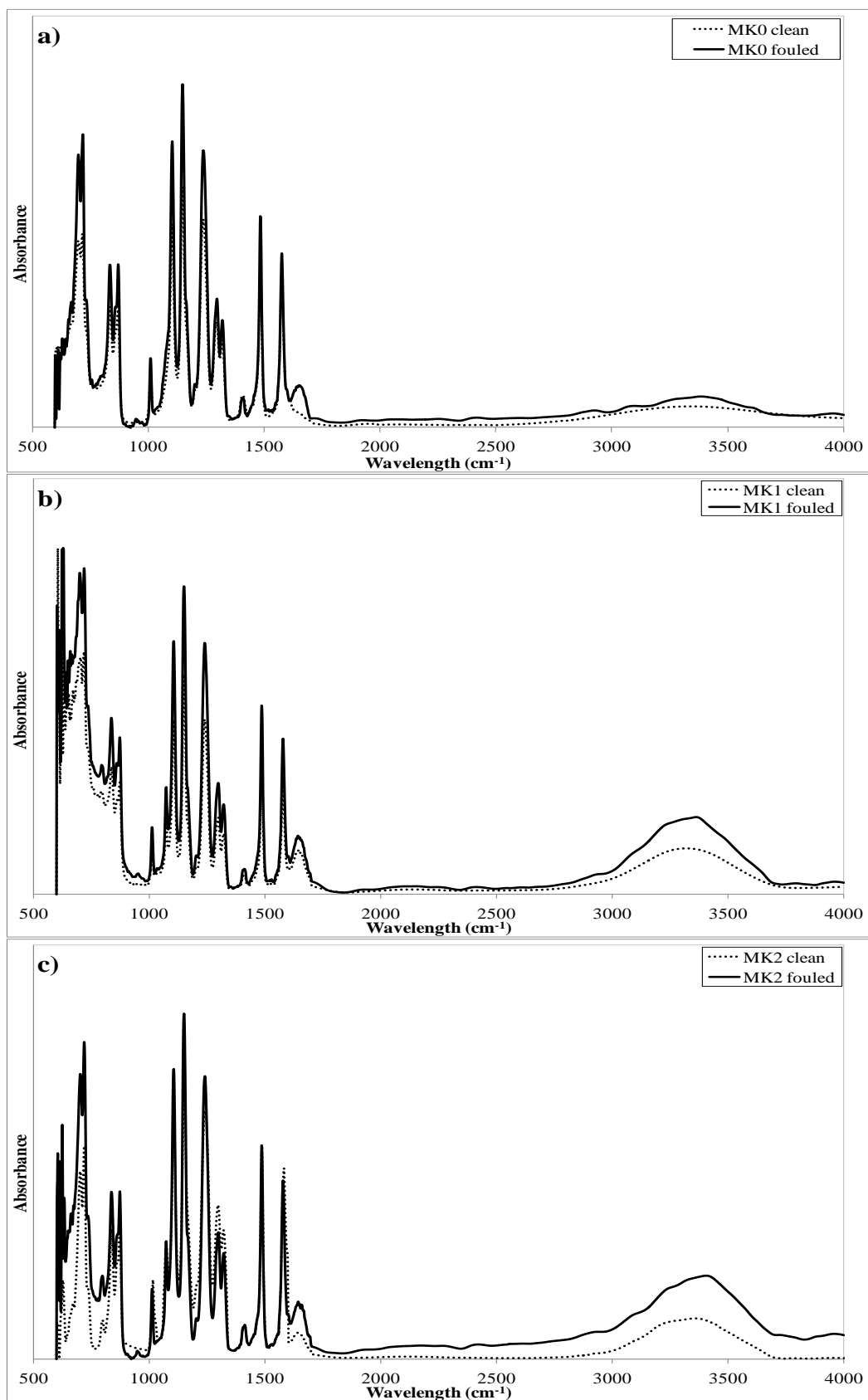


Fig. 1. FTIR-ATR spectra of the clean and fouled (a) control membranes (MK0), (b) UV-modified membranes modified in the presence of Al₂O₃ (MK1) and (c) UV-modified membranes in the presence of PEG/Al₂O₃ (MK2).

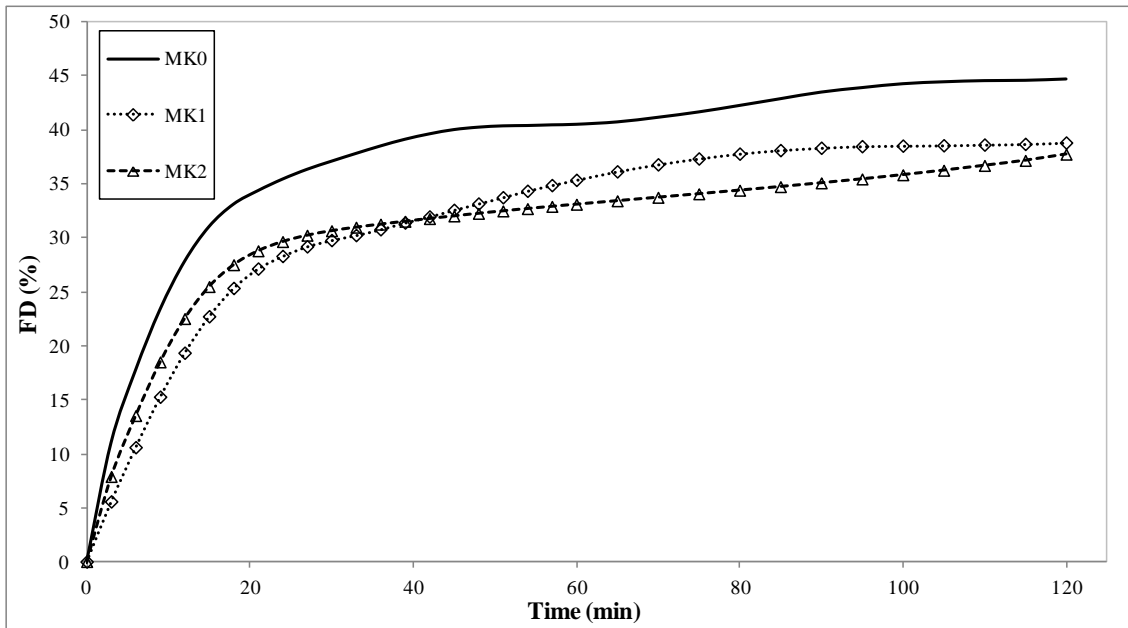


Fig. 2. Evolution of the fouling degree parameter (FD) of each membrane in TOPW ultrafiltration at 200 kPa, 1.39 m/s and 25 °C.

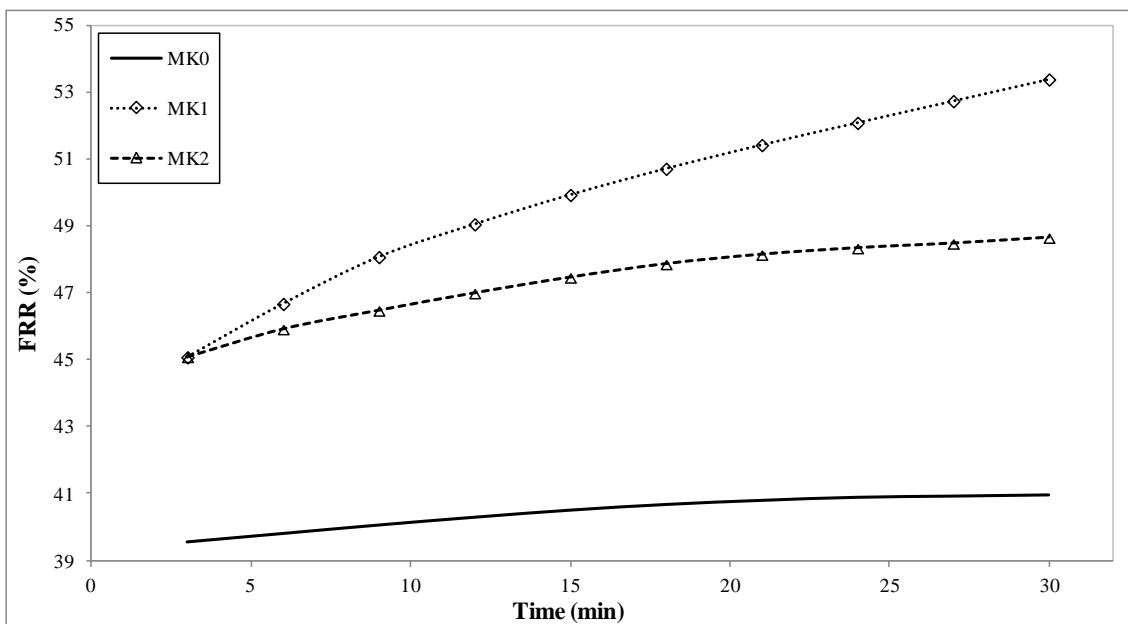


Fig. 3. Evolution of the flux recovery ratio (FRR) of each membrane in TOPW ultrafiltration at 200 kPa, 2.08 m/s and 25 °C.

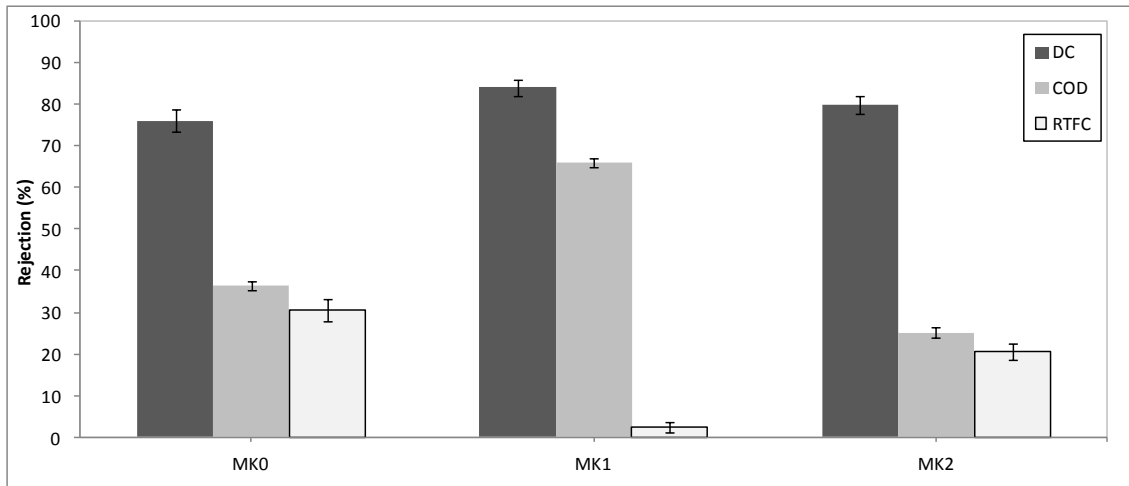


Fig. 4. Evolution of decolourisation (DC) and the rejection ratios of chemical oxygen demand (COD) and total phenolic content (TPC) of each membrane in TOPW ultrafiltration at 200 kPa, 1.39 m/s and 25 °C.