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Additional Information

1 **Fractionation of secondary effluents of wastewater treatment plants in view of the**  
2 **evaluation of membrane fouling in a further ultrafiltration step**

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8

9 **Abstract**

10 BACKGROUND: Ultrafiltration is used as tertiary treatment in wastewater treatment  
11 plants (WWTP) for wastewater reclamation. However, membrane fouling is the main  
12 drawback of the process. In this work a new effluent organic matter fractionation  
13 procedure with adsorption resins (XAD-8, XAD4 and IRA-958) has been applied  
14 without recovering the adsorbed fractions. In this way, strong and weak hydrophobic  
15 and charged hydrophilic substances of the dissolved organic matter (DOM) were  
16 removed for further ultrafiltration, in order to know the most fouling fraction. For it,  
17 secondary effluents of two WWTP and two membranes with different molecular weight  
18 cut-offs (100 kDa and 3 kDa) were used in ultrafiltration experiments in a laboratory  
19 plant.

20 RESULTS: The hydrophobic substances (especially the strong hydrophobics)  
21 predominated over the hydrophilic compounds. Membrane fouling was higher for the  
22 membrane with the highest molecular weight cut-off (100 kDa). Thus, flux decline was  
23 around 25-47% higher than that measured for 3 kDa membrane. The charged

24 hydrophilic substances (CHi) were identified as the most fouling compounds with 100  
25 kDa membrane. Reversible fouling was predominant.

26 CONCLUSIONS: The proposed fractionation system enabled to know the contribution  
27 of the different fractions to the DOM.

28

29 **Keywords:** Waste-water; Fouling; Chemical Analysis; Ultrafiltration

30

## 31 1. INTRODUCTION

32 The increasing drought has led some countries, including Spain, to reuse to a higher  
33 extent treated wastewater in agriculture. As the quality of the secondary effluent (SE) of  
34 the wastewater treatment plants (WWTP) does not meet the standards regulated by the  
35 legislation, a tertiary treatment is needed. The conventional treatment consisting of  
36 coagulation-flocculation, settling, filtration and disinfection by UV-radiation is the most  
37 used process combination in wastewater reclamation. Nevertheless, other techniques  
38 like ultrafiltration (UF) are also used in some facilities to treat the SE.<sup>1</sup> In a next future,  
39 more stringent standards will have to be accomplished due to the necessity of  
40 eliminating some persistent organic compounds that could be dangerous for the  
41 environment. UF will play a predominant role for removal of refractory pollutants like  
42 pharmaceutical substances either as only treatment or as pretreatment for other  
43 techniques like nanofiltration or adsorption.<sup>2-5</sup> The use of UF as tertiary treatment was  
44 proposed a couple of decades ago.<sup>6</sup> However, this technique has not been implemented  
45 to the expected extent. One of the reasons that can explain it is undoubtedly the main  
46 operating problem of the membranes, i.e. membrane fouling.<sup>7</sup>

47 It is clear that effluent organic matter (EfOM) is the main responsible for the membrane  
48 fouling.<sup>8-10</sup> In this way, studies on its composition and on which fractions produce the  
49 most severe fouling seem to be fundamental for predicting the UF membrane fouling in  
50 the treatment of SE. Unlike characteristics of natural organic matter (NOM) have been  
51 assessed by a great number of researchers,<sup>11,12</sup> EfOM has been less studied. According  
52 to Shon et al.,<sup>13</sup> EfOM mainly consists of soluble microbial products (SMP),  
53 anthropogenic organic compounds that are not degraded by the biomass in WWTP and  
54 NOM coming from tap water. EfOM is more difficult to be studied than NOM. For  
55 example, the properties of EfOM will mostly depend on the biological process used in  
56 WWTP, season, climate and geology of the wastewater source.<sup>14</sup>

57 Fractionation of EfOM is based on the techniques used for NOM fractionation. These  
58 techniques were firstly studied by Leenheer,<sup>15</sup> who reported in a more recent paper the  
59 way of fractionating DOM included in NOM in four main fractions (colloidal,  
60 hydrophobic, amphiphilic and hydrophilic).<sup>16</sup> Hydrophobic and hydrophilic organic  
61 matter were divided into neutrals, bases and acids. Focusing on EfOM, Imai et al.<sup>17</sup>  
62 fractionated EfOM in six fractions, which coincided with those reported by Leenheer  
63 for NOM (Hydrophobic and hydrophilic neutrals, bases and acids). The procedure  
64 mainly consisted of three adsorption steps with resins (non ionic, cationic exchange,  
65 anionic exchange). Zheng et al.<sup>18</sup> fractionated EfOM by means of a procedure including  
66 filtration (1.2 microns), 3 adsorption steps by resins and dialysis in order to obtain 5  
67 fractions (colloids, hydrophobic neutrals, hydrophobic acids, transphilic acids and  
68 neutrals, hydrophilic organic fraction).

69 Each of these components or fractions will contribute differently to membrane fouling  
70 due to individual properties, for example, hydrophobicity and charge.<sup>19</sup> The success of  
71 the fractionated methodology decreases with the number of separated fractions. In

72 addition to it, a major problem with these techniques occurs when organic matter  
73 compounds irreversibly adsorb onto the resin and consequently these fractions cannot  
74 be recovered.<sup>20</sup> In this way, it is needed to carry out a procedure ensuring that the  
75 further study of membrane fouling can guarantee reproducible results and that the  
76 procedure can be used as a tool to compare the composition of EfOM from different  
77 WWTPs. In this work, adsorption resins have been used to separate different fractions  
78 from the SE. UF experiments using SE after filtration through 5 and 0.45  $\mu\text{m}$  filters and  
79 effluents without one, two or three of the DOM fractions, which were removed with  
80 adsorption resins, were performed. These experiments allowed studying which of these  
81 effluents was the most fouling one. It means that the separated fractions were not  
82 recovered, avoiding the above mentioned desorption problems. In addition,  
83 fractionation and UF experiments were applied to effluents of two WWTPs, which  
84 make possible the comparison between different EfOMs.

85

## 86 **2. MATERIALS AND METHODS**

### 87 **2.1. Secondary effluent samples**

88 Experiments were carried out using samples from two different WWTPs. Two samples  
89 of WWTP-1 were processed (SE1 and SE1'). WWTP-1 mainly treats municipal  
90 wastewater and its performance is very high, yielding low values of COD in the SE.  
91 WWTP-2 treats municipal wastewater but the effluents of a nearby industrial area are  
92 also discharged in the WWTP. The COD values of these secondary effluents (SE2 and  
93 SE2') were higher than the COD of the effluents from WWTP-1. SE<sub>i</sub> and SE<sub>i</sub>' were  
94 taken in winter and summer, respectively. All the samples were filtered with acetate

95 cellulose filter of 5 $\mu$ m, previously to their analysis and fractionation. Table 1 shows a  
96 comparison of SE characteristics.

97 **Table 1. Characteristics of the secondary effluents used in the experiments**

PARAMETERS	SE1	SE1'	SE2	SE2'
pH	7.7	7.8	7.8	7.9
Conductivity (mS $\cdot$ cm <sup>-1</sup> )	1.82	1.98	2.15	5.70
COD (mg $\cdot$ L <sup>-1</sup> )	42.8	37.5	61.6	62.6
SUVA <sub>254</sub> (L $\cdot$ mg <sup>-1</sup> $\cdot$ m <sup>-1</sup> )	0.92	1.87	0.78	0.63

98

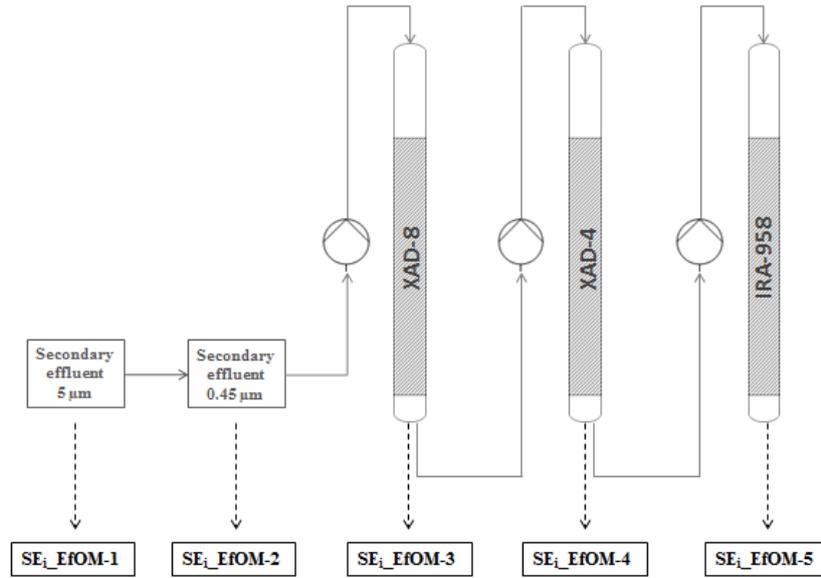
99

## 100 **2.2. Fractionation**

101 The fractionation procedure, based on the procedure proposed for NOM by Dong et al.,  
102 <sup>21</sup> consisted of 4 stages: 1) Filtration (0.45  $\mu$ m) in order to separate the non-dissolved  
103 organic matter from the different SE. 2) Strong hydrophobic organic matter separation  
104 through non-ionic resin XAD-8. 3) Weak hydrophobic (transphilic) organic matter  
105 separation with non-ionic resin XAD-4. 4) Separation of charged hydrophilic organic  
106 matter through anionic exchange resin IRA-958.

107 Filtration process was carried out with acetate cellulose filter. The pH of filtered SE<sub>i</sub>  
108 was adjusted to 2 (with 37% HCl) after XAD-8 resin adsorption and was maintained  
109 during XAD-4 adsorption. However, effluent pH was increased to 8 again (with 40%  
110 NaOH) before entering IRA-958 resin. 3 L of each fraction were obtained to perform  
111 the ultrafiltration experiments.

112 The three resins were supplied by Sigma-Aldrich. A scheme of the whole separation can  
113 be observed in Figure 1.



114

115

**Figure 1. Scheme of the whole fractionation process**

116

117 From the filtration and separation operations of the above explained fractionation  
 118 process 5 types of samples were obtained. The identification of each sample was SE<sub>i</sub>-j,  
 119 where “i” refers to WWTP from which the sample has been taken and ”j” refers to the  
 120 type of sample according to the carried out separations. Table 2 helps understanding the  
 121 meaning of the subscript ”j” including more details about the separations step.

122

**Table 2. Organic matter fractionation processes**

Fractionated samples	Operations carried out for fractions separation	Effluent characteristics
SE <sub>i</sub> -1	Filtration 5 μm	
SE <sub>i</sub> -2	Filtration 0.45 μm	SE without particulate material
SE <sub>i</sub> -3	Filtration 0.45 μm + XAD-8	SE without strong hydrophobic organic matter
SE <sub>i</sub> -4	Filtration 0.45 μm + XAD-8 + XAD-4	SE without strong hydrophobic and weak hydrophobic organic matter
SE <sub>i</sub> -5	Filtration 0.45 μm + XAD-8 + XAD-4 + IRA-958	SE without strong hydrophobic, weak hydrophobic and charged hydrophilic organic matter

123

124 Previously to their use, resins were pretreated to remove any organic content that could  
125 interfere with the experiments, according to the methodology proposed by Vieira et  
126 al.<sup>22</sup> This was done by immersing each of the resins in 0.1M NaOH solution for 24  
127 hours and then rinsing with 1L of deionised water. After this process, the resins were  
128 packed into the column feeding the following solutions at the top of the column: 1 L of  
129 0.1M NaOH followed by 1 L of 0.1N HCl, ending with 1 L of deionised water. The  
130 final 40 mL obtained after the washing was collected as a 'blank', which COD had to be  
131 below 2 mg·L<sup>-1</sup>, so that the resin could be used in the fractionation.

132 All the effluents were fed at the top of the columns using a peristaltic pump (Figure 1)  
133 at a rate of 5 mL·min<sup>-1</sup>. On the other hand, the packed resin amount necessary to  
134 achieve the correct fractionation process was related to the effluent volume and their  
135 COD. In this way, 0.23 g of resin for each g of COD was necessary in order to obtain 3  
136 L of each fraction according to previous tests carried out (data not shown).

137

### 138 **2.3. Ultrafiltration experiments**

139 Plane membranes were used for the UF experiments. Membranes were located in a  
140 Rayflow module (ORELIS, France). The tests were carried out using one membrane of  
141 100 cm<sup>2</sup> of active surface. Two commercial membranes, UC100 and FORM003Ray,  
142 were used to perform the experiments with SEi and SEi', respectively. The main  
143 membranes characteristics can be observed in Table 3.

144 Pristine membranes were used in every test. Each membrane was firstly washed to  
145 remove the preservation solution and then membrane permeability was measured using  
146 deionised water. Membranes with anomalous permeability were discarded.

**Table 3. Characteristics of the UF membranes**

	<b>UC100</b>	<b>FORM003Ray</b>
Supplier	Microdyn-Nadir	Orelis
Configuration	Plane	Plane
Active layer material	Regenerated cellulose	Polyethersulfone
Molecular weight cut-off	100 kDa	3 kDa
pH range	1–11	3 –14

148

149 The UF experiments to evaluate the membrane fouling with the different SE<sub>i</sub>-j were  
 150 carried out at a transmembrane pressure (TMP) of 2 bar, a feed flow rate of 300 L·h<sup>-1</sup>  
 151 and a temperature of 25°C. All the tests were performed with 3 L of sample, recycling  
 152 both permeate and retentate streams to the feed tank. Experiments were performed until  
 153 stationary permeate flux was reached. pH of SE<sub>i</sub>-3 and SE<sub>i</sub>-4 (pH=2 to perform the  
 154 fractionation process) was adjusted with 40% NaOH to original SE pH in order to  
 155 compare all the UF results properly. Membrane flux was determined periodically by  
 156 measuring the elapsed time to collect a particular permeate volume, during the fouling  
 157 test carried out.

158 After fouling step, membrane was rinsed during 30 minutes with deionised water  
 159 without applying TMP. After this operation, permeability was measured again in order  
 160 to find out the flux recovered by the rinsing, in other words, to calculate the reversible  
 161 fouling. All the experiments were carried out twice and fluxes reported are the mean  
 162 values obtained. If the results of the replication were not similar to the first tests, the  
 163 experiment was repeated again. Anyway, it was observed that results were completely  
 164 reproducible.

165

166 **2.4. Contact angle measurement**

167 The contact angle (right and left) of extra pure water drop (3  $\mu\text{L}$ ) on the pristine  
168 membrane surface of UC100 and FORM003Ray was measured. For each membrane 10  
169 replicates were performed, varying the locations along each cut. Results are presented as  
170 average contact angle of these replicates with their standard deviation. Measurements  
171 were carried out with the OCA 20 instrument from Data Physics Instruments  
172 (Germany).

173

174 **2.5. Samples characterization**

175 The SE of two WWTP and the different samples obtained from filtration and  
176 fractionation procedures were characterized by measuring COD, total organic carbon  
177 (TOC), UV absorbance at 254 nm ( $\text{UV}_{254}$ ), pH and conductivity. COD and TOC were  
178 measured with kits from Merck and Spectroquant® NOVA.  $\text{UV}_{254}$  absorbance was  
179 measured with a spectrophotometer DR600 from Hach Lange. pH and conductivity  
180 were measured with a pH-meter GLP 21+ and a EC-Meter GLP 31+, respectively. Each  
181 parameter was measured by triplicate.

182 Specific UV Absorbance ( $\text{SUVA}_{254}$ ), expressed in  $\text{L}\cdot\text{mg}^{-1}\cdot\text{m}^{-1}$ , was calculated as the  
183 quotient between  $\text{UV}_{254}$  ( $\text{m}^{-1}$ ) and TOC ( $\text{mg}\cdot\text{L}^{-1}$ ). This parameter is related to  
184 hydrophobic substances with unsaturated carbon bonds and aromatic groups like humic  
185 and fulvic acids.<sup>23,24</sup> Thus,  $\text{SUVA}_{254}$  increases when the concentration of these  
186 substances also increases.

187

188

189 **3. RESULTS**

190 **3.1. Characterization of filtrated and fractionated samples**

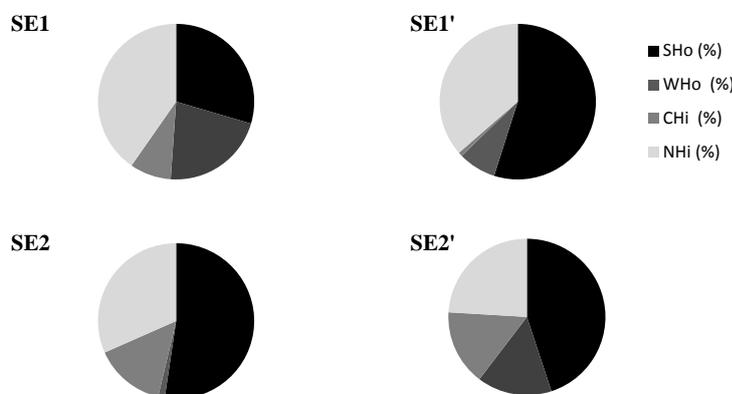
191 Table 4 shows the characteristics in terms of COD and SUVA<sub>254</sub> of all the samples  
 192 obtained for the four SE.

193 **Table 4. Filtrate and fractionated samples characterization: average COD (mg·L<sup>-1</sup>) and SUVA<sub>254</sub>**  
 194 **(L·mg<sup>-1</sup>·m<sup>-1</sup>) with their standard deviations.**

	SE1		SE1'		SE2		SE2'	
	COD	SUVA <sub>254</sub>						
SEi-1	42.8 ± 0.3	0.92 ± 0.02	37.5 ± 0.1	1.87 ± 0.11	61.6 ± 0.5	0.78 ± 0.06	62.6 ± 0.3	0.63 ± 0.04
SEi-2	36.2 ± 0.4	0.79 ± 0.08	35.7 ± 0.7	1.97 ± 0.12	51.2 ± 1.1	0.71 ± 0.06	47.4 ± 0.9	1.38 ± 0.03
SEi-3	25.5 ± 0.1	0.76 ± 0.10	16.1 ± 0.3	1.22 ± 0.08	24.4 ± 0.4	0.52 ± 0.05	26.1 ± 0.7	0.65 ± 0.10
SEi-4	17.7 ± 0.2	0.73 ± 0.22	13.3 ± 0.4	0.70 ± 0.03	23.7 ± 0.3	0.37 ± 0.02	18.8 ± 0.2	0.53 ± 0.08
SEi-5	14.6 ± 0.2	0.42 ± 0.04	13.0 ± 0.1	0.77 ± 0.05	16.2 ± 0.1	0.34 ± 0.05	11.4 ± 0.2	0.56 ± 0.05

195

196 Figure 2 illustrates the contribution to DOM (organic matter of SEi-2) of the 4 separated  
 197 fractions: strong hydrophobic (SHo = SEi-2 – SEi-3), weak hydrophobic (WHo = SEi-3  
 198 – SEi-4), charged hydrophilic (CHi = SEi-4 – SEi-5) and neutral hydrophilic (NH<sub>i</sub> =  
 199 organic matter of SEi-5). This contribution has been calculated in percentage of  
 200 removed COD with respect to COD of DOM.



201

202

**Figure 2. Fractionated samples contribution of the DOM**

203 The graphics display that the predominant substances in DOM were the hydrophobic  
204 ones (sum of strong and weak hydrophobic substances), irrespective of SE considered.

205 In WWTP-1 the COD of DOM from the two SE were very similar (36.2 and 35.7 for  
206 SE1-2 and SE1'-2, respectively). However, SHo substances concentration was very  
207 different as it can be observed in Figure 2. Thus, the contribution of SHo to DOM in  
208 SE1' was considerably higher than in SE1.  $SUVA_{254}$  parameter, whose value is related  
209 to the aromatic compounds like humic acids belonging to SHo substances, confirms this  
210 result. WHO and CHi percentages also varied in both SE of WWTP-1, while NHi  
211 percentages in DOM were similar (40.3% and 36.4% for SE1 and SE1', respectively).  
212 Tag et al.<sup>26</sup> carried out a similar DOM fractionation for EfOM of two membrane  
213 bioreactors. Their results showed slightly higher percentages of NHi (42.0-48.9%) than  
214 those obtained for SE1 and SE1'. However, these authors reported that the  
215 concentrations of hydrophilic substances (CHi+NHi) were higher than the  
216 concentrations of the hydrophobic organic matter (SHo+Who), contrary to the results  
217 presented in this work. On the contrary, Zheng et al.<sup>18</sup> reported that the hydrophobic  
218 substances predominated over the hydrophilic ones.

219 In WWTP-2 SHo and CHi percentages were similar in both samples, meanwhile WHO  
220 in SE2' was higher than in SE2.

221 According to the amounts of aromatic non-biodegradable compounds in all the SE,  
222 which are related to  $SUVA_{254}$  data, it can be commented that the values measured for  
223 the samples taken in summer season (SEi'-2) were the highest. On the other hand, these  
224  $SUVA_{254}$  values of SE1'-2 and SE2'-2 were reduced after adsorption with XAD-8 resin  
225 in percentages of 38.1% and 52.9%, respectively.

226 It has to be highlighted that different results achieved for the samples taken from the  
227 same WWTP (with similar initial COD) are not attributed only to the different season  
228 when the samples were taken, but also to the change of the operating parameters  
229 (organic loading rate, sludge retention time, dissolved oxygen concentration). Tian et  
230 al.<sup>25</sup> studied the seasonal variation of EfOM characteristics of a WWTP in Berlin. These  
231 authors found significant differences in the samples characteristics in terms of SMP  
232 concentrations. In this way, it has always been expected a significant different  
233 contribution of the organic matter fractions to the total EfOM.

234

## 235 **3.2. Ultrafiltration experiments**

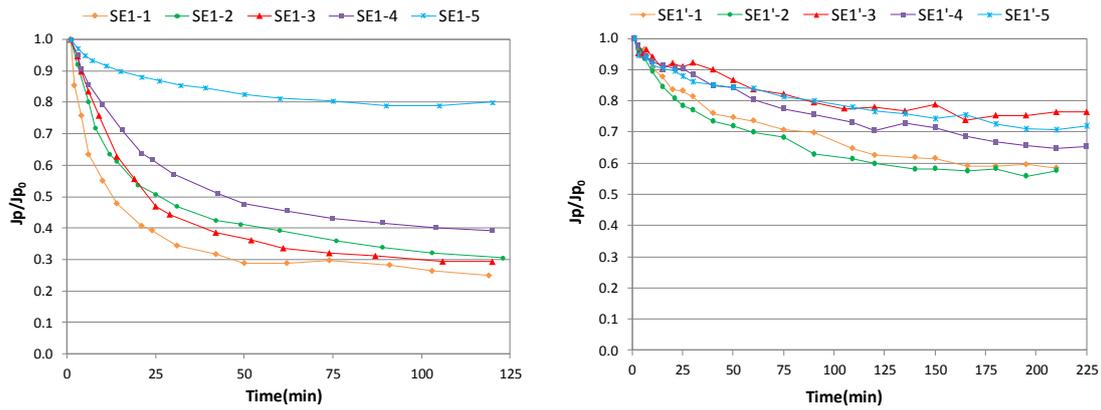
### 236 ***3.2.1. Contact angle of the tested membranes***

237 The contact angle of a membrane is related to its hydrophilicity and it depends on  
238 membrane material and porosity.<sup>27</sup> The values obtained for UC100 and FORM003Ray  
239 were  $27.4 \pm 12.0^\circ$  and  $62.1 \pm 3.1^\circ$ , respectively. These values confirmed that UC100 was  
240 more hydrophilic than FORM003Ray. These measurements are of great interest in order  
241 to relate EfOM composition to the membrane fouling, as it will be explained in the  
242 following sub-sections.

243

### 244 ***3.2.2. WWTP-1***

245 Figure 3 summarizes UF tests results, in terms of evolution of normalized flux  
246 (permeate flux of fouling experiment divided by the initial one,  $J_p/J_{p0}$ ) over time, for the  
247 five effluents of both SE of two WWTP-1 samples using UC100 and FORM003Ray  
248 membranes.



249  
250 **Figure 3. WWTP-1: Fouling UF test with UC100 membrane (left chart) and FORM003Ray**  
251 **membranes (right chart)**

252

253 It can be observed that membrane fouling was considerably higher in the experiments  
254 with UC100 membrane. It means that the membrane cut-off is the most important  
255 parameter to be considered to explain the more severe fouling of this membrane.  $J_p/J_{p0}$   
256 ratio went down to 0.24 at the end of the experiment with UC100 for the rawSE, which  
257 is a similar value to that obtained by Laabs et al.<sup>10</sup> These authors also worked with a  
258 regenerated cellulose UF membrane of 100 kDa (YM100 from AMICON) with EfOM  
259 from Boulder WWTP. In this way, substances with molecular weights similar to the  
260 membrane cut-off block the membrane pores reducing the permeate flux very quickly.  
261 On the contrary, when 3 kDa membrane was used,  $J_p/J_{p0}$  ratio diminished only to 0.6.

262 Focusing on the tests with UC100 membrane, it can be observed that the normalized  
263 flux increased as water fractions were separated. It is clear that the membrane fouling  
264 will depend on both the COD and the type of organic matter in the sample. Only SHo  
265 substances seemed to hardly contribute to the membrane fouling since the permeate flux  
266 did not changed when SHo compounds were previously separated (comparing green and  
267 red lines). It may be probably due to the fact that the concentration of these substances  
268 in EfOM was small in SE1. On the other hand, the highest flux difference on the

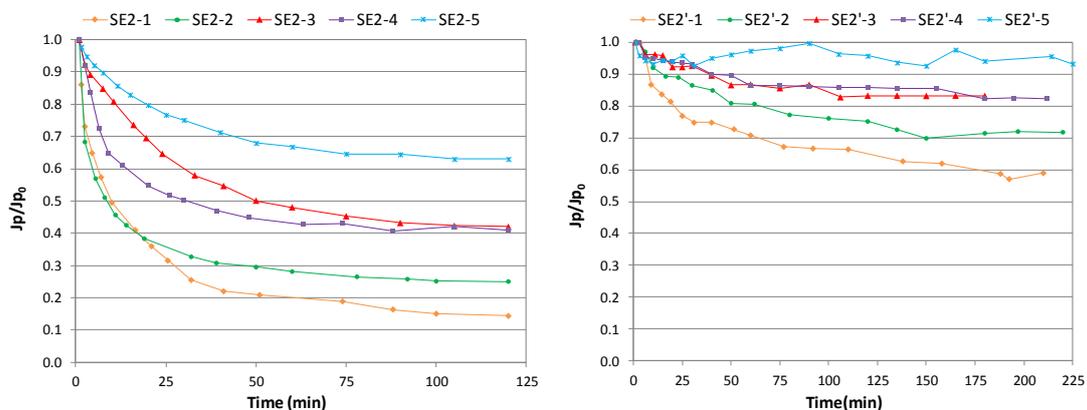
269 stationary conditions was found when SE1-5 was ultrafiltered. It indicates that the CHI  
 270 organic matter was a highly fouling fraction, in spite of COD of this fraction, which was  
 271 the smallest one (Figure 2). This can be related to the high hydrophilic character of  
 272 UC100 membrane, showing high affinity for CHI substances. Finally, the lowest fouling  
 273 was achieved for the effluent without SHo, WHO and CHI, reaching  $J_p/J_{p0}$  ratio values  
 274 around 0.80 at the end of the experiment.

275 Unlike UC100 membrane, FORM003Ray fouling decrease when SHo compounds were  
 276 eliminated, which may be due both to their high concentration in SE1' and to the greater  
 277 affinity towards hydrophobic substances of FORM003Ray membrane. The COD of  
 278 WHO and CHI fractions were very low, then the normalized flux on the stationary  
 279 conditions of SE1'-4 and SE1'-5 were very similar to SE1'-3.

280

### 281 3.2.3. WWTP-2

282 Figure 4 represents the evolution of normalized flux over time for the five effluents of  
 283 both SE of two WWTP-2 using UC100 and FORM003Ray membranes.



284

285 **Figure 4. WWTP-2: Fouling UF test with UC100 membrane (left chart) and FORM003Ray**  
 286 **membranes (right chart)**

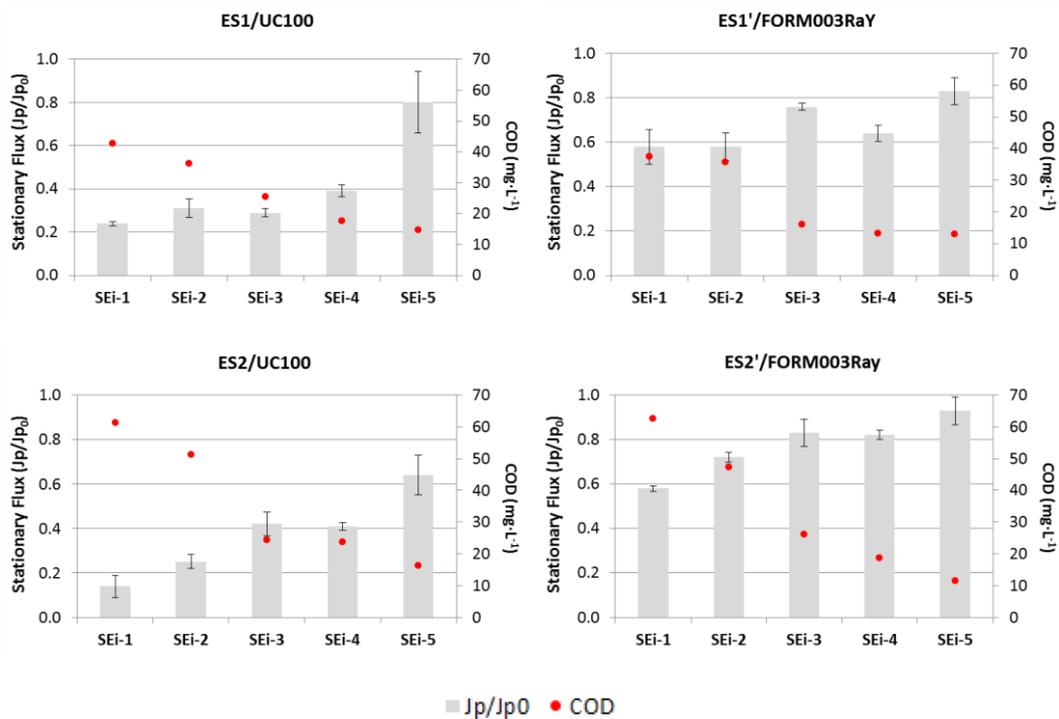
287

288 In this case, as the samples of WWTP-1, the membrane fouling observed by  $J_p/J_{p0}$   
289 diminution was much higher for UC100 than for FORM003Ray membranes. However,  
290 hydrophilic compounds also played a relevant role in UC100 membrane fouling and  
291 both CHi and also NHi compounds seem to be a higher fouling effect than that observed  
292 in WWTP-1. In this way,  $J_p/J_{p0}$  ratio values in effluent that contain CHi and NHi (SE2-  
293 4) achieved similar values to those measured in WWTP1 (around 0.41 in both SEi-4).  
294 Meanwhile, effluent without CHi (SE2-5) compounds produced more fouling than that  
295 observed in WWTP-2, whose  $J_p/J_{p0}$  ratio at the stationary conditions reached a value of  
296 0.64 in front of 0.80 achieved to SE1-5. Unlike WWTP-1, SHo substances had high  
297 fouling capacity, as the final  $J_p/J_{p0}$  for the effluent without these compounds (SE2-3)  
298 was higher than the final  $J_p/J_{p0}$  for the effluent with them (SE2-2). This fact was due to  
299 the high contribution of these substances to COD of EfOM. On the contrary, COD of  
300 WHO fraction was negligible, which is explained by the fact that its separation did not  
301 modified the permeate flux of UC100 membrane (comparing red and purple lines).

302 The fouling tests with FORM003Ray showed that the membrane fouling decreased as  
303 EfOM fractions were separated, except for WHO fraction, since the flux decline with  
304 and without these substances was very similar (similar behavior in the test with UC100  
305 membrane), despites COD contribution was not negligible. As for WWTP-1, the lowest  
306 fouling was achieved for the effluent without hydrophobic and CHi substances (SE2'-  
307 5), reaching  $J_p/J_{p0}$  ratio value around 0.94, which can be explained by the more  
308 hydrophobic character of FORM003Ray membrane.

309 Summarizing, it can be commented that the most important parameter in UF membranes  
310 fouling was their molecular weight cut-off. Even under different EfOM characteristics,  
311 the membrane with the lowest cut-off (FOR0003Ray) yielded the lowest flux decay  
312 with the time. In addition, the fouling effect of hydrophilic compounds, especially in the

313 experiments with the more hydrophilic membrane (UC100), was higher than the fouling  
 314 effect of hydrophobic compounds. In this way, the final  $J_p/J_{p0}$  increased when CHI  
 315 substances were removed. Among hydrophobic compounds, WHO fraction hardly  
 316 influenced on the membrane fouling caused by EfOM. Figure 5 illustrates these  
 317 conclusions relating the effluent COD of samples treated to their final  $J_p/J_{p0}$  ratio values  
 318 (average values of the last three normalized flux values in the experiments). On the  
 319 other hand, it has to be highlighted that the final COD of DOM when the three fractions  
 320 were removed (SEi-5 stream) was similar in the four SE, reaching a final value of  $13.8$   
 321  $\pm 2.1$ , regardless of the initial COD.



322

323

**Figure 5. Stationary permeate flux and COD of the different effluents fractionated.**

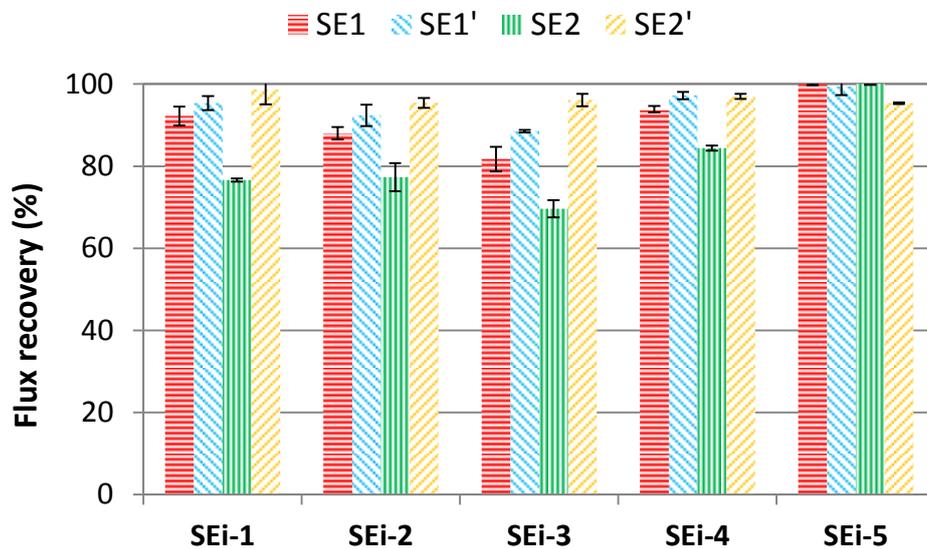
324

325

326

327 **3.2.4. Fouling reversibility**

328 Figure 6 shows the percentages of permeate flux recovered after rinsing for all UF  
329 experiments. In general terms, it can be observed that the reversible fouling  
330 predominated over the irreversible one. On the other hand, the flux recovery in the tests  
331 performed with UC100 membrane was lower than that achieved with FORM003Ray  
332 membrane. It was expected, since the high molecular weight cut-off of UC100  
333 membranes enable the penetration of organic matter compounds that may adsorb within  
334 the pores, driving to irreversible fouling.



335

336 **Figure 6. Recovery of permeate flux after rinsing in the UF experiments with all the samples**

337

338 Concerning the different organic matter fractions, the samples with only NHi substances  
339 (SEi-5) showed the highest flux recovery, with values above 95%. This DOM fraction  
340 has high molecular weight components such as polysaccharides and proteins,<sup>26,28</sup> which  
341 led to membrane surface fouling instead of pore blocking, explaining in this way the  
342 reversible fouling. The size of the other EfOM fractions is smaller than that of NHi  
343 compounds, enhancing internal pore blocking and consequently the irreversible

344 membrane fouling. This phenomenon was more important for UC100 membrane than  
345 for FORM003Ray membrane due to its greater cut-off, as commented above.

346

#### 347 **4. CONCLUSIONS**

348 There is no doubt that membrane fouling is the main problem associated to the  
349 application of UF process to secondary effluents. The study of EfOM and the fouling  
350 potential contributed to a better understand of the membrane fouling and to prevent it.

351 In this work, successive separation of the organic matter fractions has been successfully  
352 used as an alternative of the fractions isolation and further re-dissolution for UF tests  
353 performance. From the carried out tests, it can be concluded that organic matter  
354 fractions of SE from the same WWTP vary along the time. For SE ultrafiltration the  
355 main fouling factor was the membrane cut-off. Thus, the flux decline of samples (SEi-1  
356 to SEi-4) with 100 kDa membrane was between 25% and 47% higher than that obtained  
357 with 3 kDa membrane. The potential fouling of different DOM fractions had more  
358 significance in UC100 membrane and the most foulant fraction for this membrane was  
359 CHi compounds. In addition to it, reversible fouling predominated over irreversible one  
360 (above all in UF tests with 3 kDa membrane) and flux recovery with a rinsing becomes  
361 almost 100% once CHi fraction had been separated.

362

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366

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