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1 **Antifouling grafting of ceramic membranes validated**  
2 **in a variety of challenging wastewaters**

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25 **Abstract**

26 Compared to traditional separation and purification techniques, membrane filtration is particularly  
27 beneficial for the treatment of wastewater streams such as pulp and paper mill effluents (PPME),  
28 olive oil wastewater (OOWW) and oil/gas produced water (PW). However, severe membrane  
29 fouling can be a major issue.

30 In this work, the use of ceramic membranes and the potential for the broad applicability of a  
31 recently developed antifouling grafting was evaluated to tackle this issue. To this end, the fouling  
32 behavior of native and grafted membranes was tested in the selected difficult wastewater streams,  
33 both in dead-end and in cross-flow mode. In addition, the quality of the produced permeate water  
34 was determined to assess the overall performance of the investigated membranes for reuse or  
35 recycling of the treated wastewater.

36 The obtained results show that grafting significantly enhances the antifouling tendency of the  
37 ceramic membranes. Particularly, the membrane grafted with methyl groups using the Grignard  
38 technique (MGR), showed in all cases no or negligible fouling as compared to the native  
39 membrane. As a consequence, the process flux or filtration capacity of the MGR membrane in  
40 cross-flow is always higher and more stable than the native membrane, even though the grafting  
41 lowers the pure water flux. Hence, the inert character of the MGR membrane is repeatedly proven  
42 and shown to be broadly applicable and generic for anti-fouling, without loss in permeate quality.

43 Moreover, in case of OOWW, the quality of the MGR permeate is even better than that of the  
44 native membrane due to its lower fouling. All results can be explained taking into account the  
45 physico-chemical properties of foulants and membranes, as shown in previous work. In conclusion,  
46 the use of MGR membranes could provide an optimum economical solution for the treatment of  
47 the selected challenging wastewaters.

48

49

50 **Key words:**

51 Pulp and paper waste effluents, olive oil wastewater, oil/gas produced water, ceramic membranes,  
52 membrane fouling, and antifouling grafting

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## 57 **1. Introduction**

58 The production of wastewater is unavoidable, as water is a vital part of operational processes in  
59 different types of industries. The increasing demand of water for industrial use, originating from  
60 increasing economic activity (UNESCO, 2012) and the prompt industrial growth, has led to plenty of  
61 wastewater production every year (Chakrabarty et al., 2008; Cheryan and Rajagopalan, 1998; Ju et  
62 al., 2008; Lin and Lan, 1998; Yusoff and Murray, 2011; Zaidi et al., 1992; Zhu et al., 2014). This  
63 wastewater is one of the biggest threats for water supply worldwide. The reliable key factor for  
64 diminishing the water scarcity would be the purification or treatment of industrial wastewater  
65 (McCloskey et al., 2010; Morales Chabrand et al., 2008; Cambiella et al., 2007).

66 In this work, we focus on three important industrial wastewater streams: 1) pulp and paper mill  
67 effluents, 2) olive oil wastewater and 3) oil/gas produced water (wastewater produced during the  
68 pumping out of oil/gas from the earth known as produced water), which contribute extensively to  
69 the whole of industrial wastewater in the world. These industrial wastewater streams are not only  
70 large in quantity, but they are also very difficult to treat because of their complex chemical  
71 composition.

72 **Pulp and paper mill effluents (PPME):** Pulp and paper production is a water-intensive process.  
73 Paper industry ranks third in the world after metal and chemical industries in terms of fresh water  
74 consumption and wastewater creation (Beril Gnder et al., 2011). At present, a number of pulp and  
75 paper mills treat their wastewater by biological treatment systems. However, after the biological  
76 treatment, the effluent still contains significant amounts of microorganisms, dyes and suspended  
77 solids. In addition, inorganic compounds cannot be removed effectively by biological treatment.  
78 Moreover, the pulp and paper mills generate a variety of pollutants depending upon the type of  
79 the pulping process, making it difficult to treat wastewater by biological treatment.

80 Hence, advanced treatment is essential to improve the discharge quality of the PPME and/or to  
81 recycle it (Mnttri et al., 2006). Among the advanced treatment processes, membrane technology  
82 is an attractive alternative to treat PPME. In literature, a limited number of studies have been  
83 found dealing with membrane-based treatment of PPME. Jonsson and coworkers (Jonsson et al.,  
84 1996) reported that membrane-based treatment is suitable for removal of color from paper mill  
85 effluent; however, the composition of the color had an important influence on the membrane  
86 performance. A few other researchers also reported that the membrane separation is an  
87 appropriate technique for removal of adsorbable organic halogens, chemical oxygen demand  
88 (COD), and color from PPME (Afonso and Pinho, 1991; De Pinho et al., 2000; Mnttri et al., 2006;  
89 Zaidi et al., 1992). Pizzichini (Pizzichini et al. 2005) performed experiments using ceramic

90 microfiltration (MF), polymeric MF, ultrafiltration (UF) and reverse osmosis (RO) modules to treat  
91 the PPME wastewater with the aim of reusing the treated water in the manufacturing process.  
92 Furthermore, Mänttari (Mänttari et al., 2006) evaluated the possibilities of polymeric nanofiltration  
93 (NF) for the purification of discharge water from the activated sludge process and they reported  
94 that NF is an attractive process to purify the paper mill wastewater.

95 However, the most important limitation that appeared in PPME treatment by membrane processes  
96 is membrane fouling, causing a rapid flux decline. Lipophilic extractives are potential foulants for  
97 membrane applications, which are abundantly present in PPME (Dal-Cin et al., 1996; Ragona et al.,  
98 1998; Ramamurthy et al., 1996). Flux decline caused by the irreversible adsorption of these  
99 foulants is a major problem for the economic implementation of NF for the purification and  
100 recycling of this type of wastewater.

101 **Olive oil wastewater (OOWW):** The management of OOWW is a very important issue as this is one  
102 of the major sources of pollution of the water environment, especially in Mediterranean countries.  
103 Similar to the pulp and paper production process, also the olive milling is a water intensive process,  
104 causing the OOWW to be the main by-product of the olive oil extraction (Borja et al., 1992; Erguder  
105 et al., 2000; Tsonis et al., 1989). Generally, the OOWW is characterized by high concentrations of  
106 several organic compounds, such as sugars, organic acids, polyalcohols, lipids, proteins and  
107 polyphenolic substances, which make OOWW difficult to treat (Erguder et al., 2000; Gavala et al.,  
108 1996; Jaouani et al., 2003; Rozzi et al., 1996).

109 There are different ways or methods adopted to process or dispose this wastewater. For example,  
110 disposal of the OOWW to agricultural soils (Giovacchino et al., 2002; López et al., 1996; Riffaldi,  
111 1993; Tamburino et al., 1999), natural evaporation (Cegarra et al., 1996; Fiestas Ros de Ursinos et  
112 al., 1992), thermal concentration (Fiestas Ros de Ursinos et al., 1992), treatment with lime (Aktas et  
113 al., 2001; Al-Malah et al., 2000) and oxidation (Marques et al., 1997) have been reported.  
114 Composting (Bouranis et al., 1995; Fiestas Ros de Ursinos et al., 1992; Marques, 2001) and  
115 biological treatment (Ammary et al., 2005; Borja et al., 1996; Fountoulakis et al., 2002; Marques,  
116 2001) are among the methods that are suggested most for the management of the OOWW.  
117 However, the efficiency of the process and the complexity might vary significantly. Importantly, the  
118 cost involved for processing the OOWW by these methods is quite high. As a rule, high costs is  
119 quite often the main reason for not adopting efficient treatment methods. Therefore, the OOWW  
120 treatment by traditional techniques is limited (Cheryan and Rajagopalan, 1998; Paraskeva et al.,  
121 2007).

122 Membrane technology has already been reported as a better alternative for the treatment of the  
123 OOWW (Bódalo-Santoyo et al., 2003). It offers a number of benefits such as low energy

124 consumption, no additives required, no phase changes etc. compared to the traditional techniques  
125 for irrigation or even for recycling of the OOWW (Akdemir and Ozer, 2009; Borsani and Ferrando,  
126 1996; Coskun et al., 2010; Paraskeva et al., 2007; Stoller, 2008; Turano et al., 2002). Recently,  
127 combined membrane processes for the selective fractionation, recovery and concentration of  
128 polyphenols from the OOWW also have been proposed (Paraskeva et al., 2007; Garcia-Castello et  
129 al., 2010; Russo, 2007).

130 However, fouling, not surprisingly, is again cited as the major factor that limits the application of  
131 membrane technology for the OOWW treatment (Stoller, 2013). Several approaches to mitigate  
132 this problem have been attempted (Belkacem et al., 1995; Cheryan and Rajagopalan, 1998).  
133 Nevertheless, membrane fouling still remains one of the main challenges for the implementation of  
134 membrane technology in the OOWW treatment.

135 **Produced water (PW):** Oil/gas is one of the key energy sources worldwide and its production is still  
136 indispensable to fulfil the energy demand. While oil is produced, some unfavorable environmental  
137 effects occur, e.g. PW is produced during oil production and considered the largest by-product  
138 associated with the oil production (Folarin et al., 2013; Siriverdin et al., 2004). The PW is a  
139 continuous source of contaminants to the ecosystems (Bakke et al., 2013).

140 On the other hand, the composition of the PW is very complex, having distinctive characteristics  
141 due to the presence of dispersed oil, production chemicals, corrosion products, heavy metals, large  
142 amounts of organic material, inorganic salts and natural radioactive minerals (Dyke et al., 1990;  
143 Farnand et al., 1989; Zaidi et al., 1992). In addition, characteristics of the PW usually vary  
144 significantly depending on the location of the field, produced hydrocarbon (Bakke et al., 2013) and  
145 life of the well (Kose et al., 2012). Therefore, treatment of PW is a growing challenge in all oil  
146 producing regions and its management has become a major issue for the public and regulators  
147 (Wandera et al., 2012). The large volume of the PW presents not only environmental challenges  
148 but also potential opportunities for beneficial reuse, recycling and disposal alternatives (Horner et  
149 al., 2011). Thus, it is absolutely necessary to improve innovative technologies for the treatment of  
150 the PW, not only to meet the increasingly stringent environmental regulations, but also to improve  
151 the economic viability of the processes (Xu and Drewes, 2006) and possibly leading to a new source  
152 of water.

153 In the past few decades, various conventional methods have been developed for the treatment of  
154 the PW, including biological (Li et al., 2006; Li et al., 2010), physical (Bayati et al., 2012) and  
155 chemical (Shokrollahzadeh et al., 2012) or a combination of these (Ge et al., 2014; Li et al., 2011;  
156 Younker and Walsh, 2014; Zhang et al., 2011). However, these methods are more or less energy  
157 and time consuming, suffer from low efficiency and are not effective for treating tiny oil droplets. A

158 number of reports stated that these conventional techniques can reduce oil concentration to  
159 hardly 1% by volume of the total wastewater and cannot efficiently remove oil droplets below 10  
160  $\mu\text{m}$  size. Consequently, difficult and serious problems have been raised such as water environment  
161 pollution and difficulties to generate an effluent that is appropriate for reuse(Ahmadun et al.,  
162 2009; Fakhru'l-Razi et al., 2009; Igunnu and Chen, 2012; Li et al., 2009).

163 Again, one of the important solutions for addressing these issues is the adoption of membrane  
164 technology. Ahmadun and co-worker (Ahmadun et al., 2009) provided an overview on different  
165 facets of membrane technology used for the PW treatment. In recent decades, membrane  
166 filtration of oil/water emulsions has been extensively investigated (Pan et al., 2012; Silalahi et al.,  
167 2009; Yang et al., 2011; Zhou et al., 2010), and results revealed that membrane filtration is an  
168 efficient technique to separate oil/water mixture due to its ability to effectively remove oil droplets  
169 from water (Abadi et al., 2011; Ahmadun et al., 2009; Ezzati et al., 2005; Pan et al., 2012; Silalahi et  
170 al., 2009; Sing et al., 2011). Membrane separation has already received extensive appreciations due  
171 to high retention ratios, low energy consumption, low footprint and its relatively simple  
172 operational process (Drioli and Romano, 2001; Elimelech and Phillip, 2011). In addition, membrane  
173 technology offers a potential solution to remove micron sized and even submicron size oil droplets  
174 from oily wastewater with acceptable discharge quality according to the oil and gas standards  
175 (Bilstad and Espedal, 1996; Elmaleh and Ghaffor, 1996; Santos et al., 1997; Teodosiu et al., 1999;  
176 Yang et al., 2012; Zaidi et al., 1992). Moreover, the degree of removal of the hydrocarbon  
177 contaminants by membrane filtration, especially UF, is very high, even dissolved oils are partially  
178 retained (Bilstad and Espedal, 1996; Teodosiu et al., 1999; Zubarev et al., 1999).

179 However, membranes for oil/ water separation suffer from serious fouling due to the adsorption of  
180 oil droplets on the surface and/or in the pores, causing a sharp flux decline (Kong and Li, 1999;  
181 Song, 1998). Again, innovative solutions to reduce the fouling tendency of the membranes, will be  
182 of value here.

183 **Overall**, membrane technology has been shown beneficial and has high potential to become the  
184 proper treatment for the huge quantities of wastewater belonging to the three selected types, if  
185 the membrane fouling issue can be overcome or minimized. The major objective of this study is to  
186 evaluate the potential of ceramic membranes and of the recently developed antifouling grafting on  
187 ceramic membranes (Meynen et al., 2009; Mustafa et al., 2014; Rezaei Hosseinabadi et al., 2014),  
188 to treat the chosen challenging wastewater streams. The grafting of NF membranes, especially  
189 methyl grafting using the Grignard technique, has already shown unparalleled strong antifouling  
190 effects for foulants typical for surface and ground water (Mustafa et al., 2014). In this work we  
191 want to clarify if the same positive effects are obtainable for different foulants present in a variety

192 of waste waters, and for more opener UF membranes. Moreover, we want to show the generic  
193 nature of the anti-fouling layer and consequently its broad applicability to different wastewater  
194 streams, while maintaining the permeated water quality.

195 At the end of this introduction, we want to remark that grafting of ceramic membranes is not new.  
196 Silanation and phosphonic acid grafting has been frequently used in the state of the art to modify  
197 metal oxide surfaces and/or membranes for higher hydrophobicity and/or narrowing pore size, as  
198 well described in a recent review paper (Meynen et al., 2014). Only in our previous work, the use of  
199 these functionalized surfaces has been studied as a method for decreasing the fouling tendency of  
200 ceramic membranes. To decrease the fouling of polymeric membranes, modification by grafting,  
201 plasma or other surface treatment has been explored before (Kochkodan et al., 2014; Li et al.,  
202 2014; Rana et al., 2010; Saqib et al., 2016).

203

## 204 **2. Materials and Methods**

### 205 **2.1. Membranes and chemicals**

206 Small-scale, commercially available monochannel tubular TiO<sub>2</sub> membranes with an outer diameter  
207 of 1 cm, an inner diameter of 0.7 cm, and a length of 12 cm were used. Both NF and UF membranes  
208 were utilized: the average pore diameter was 0.9 nm for the NF membranes and 30 nm for the UF  
209 membranes. All membranes were acquired from the company Inopor GmbH Germany (pore sizes  
210 as communicated by the supplier).

211 For the grafting of some of these membranes, two different grafting techniques and two different  
212 grafting groups were used (see 2.2) (Mustafa et al., 2014). The grafting reagents (i.e.  
213 methylmagnesium bromide, phenylmagnesium bromide, and methyl phosphonic acid) are supplied  
214 by Sigma Aldrich. Different model foulant solutions and real wastewaters were used to check the  
215 antifouling tendency of the grafted membranes in comparison to the native membranes: 1) real  
216 OOWW that was provided by "Cyclus ID Ltd" Spain, partner in the EU-FP7 project CeraWater; 2)  
217 Wood extract (WE) to make model solutions that mimic real PPME was supplied by another  
218 CeraWater project partner "Lappeenranta University of Technology (LUT)" Finland; 3) two model  
219 oil/water emulsions, with different types of surfactant, mimicking PW. All model foulant solutions  
220 were prepared using pure water (i.e. processed water using reverse osmosis membranes in VITO),  
221 with a conductivity of less than 15 ms/cm and pH 6.5–7. Chemicals such as hexadecane, sodium  
222 chloride, sodium dodecyl sulfate, and benzyl-dimethyl-tetradecyl-ammonium chloride to make  
223 oil/water emulsions were purchased from the chemical company MERCK. Others chemicals such as  
224 sulfuric acid and sodium hydroxide were also purchased from the chemical company MERCK.

225 Ecolab manufacturers delivered the cleaning agents such as P3 Ultrasil 110 and P3 Ultrasil 75, for  
226 cleaning the filtration system and the fouled membranes.

227

## 228 **2.2. Grafting of TiO<sub>2</sub> membranes**

229 TiO<sub>2</sub> NF and UF membranes are highly hydrophilic membranes, containing abundant -OH groups on  
230 their whole pore surface. To vary the surface chemistry of the TiO<sub>2</sub> membranes, and create  
231 antifouling effects, while maintaining a high water flux, different TiO<sub>2</sub> membranes were grafted  
232 using two different chemical grafting methods: phosphonic acids (PA) grafting and Grignard  
233 reagents (GR) grafting. Two different functional groups: methyl (M) groups and phenyl (P) groups  
234 were grafted by both PA and GR grafting methods. In all cases, the membranes were contacted  
235 (with stirring and shaking or with filtration) for several hours to the appropriate reaction mixture : a  
236 mixture of the right Grignard reagent in dry diethyl ether for GR grafting, or a mixture of the right  
237 phosphonic acid in water for PA grafting. After reaction, the membranes were washed in the  
238 proper way in order to remove byproducts or unreacted or loosely bound material. After washing,  
239 all membranes were dried at 60°C under vacuum before use in performance tests. Due to the  
240 moisture sensitivity of the Grignard reaction, this method requires a proper pretreatment of the  
241 membranes to remove the adsorbed water from the membrane surface. More details of the  
242 grafting procedures can be found in (Mustafa et al., 2014, Mustafa et al., 2016). The same  
243 procedures could be used to graft both NF and UF membranes successfully.

244 It is worth noting that even for the same functional group, both grafting techniques deliver  
245 different surface chemistries (Mustafa et al., 2014). Grignard grafting leads to a partial replacement  
246 of the surface -OH groups of the native membranes, and to a unique direct bond of the organic  
247 groups to the metal atom (-M-R) not involving an oxygen atom (Meynen et al., 2009). Chemical  
248 characterization (IR, NMR, TGA-MS) of Grignard grafted powders (Pieter Van Heetvelde et al.,  
249 2013) and membranes (Rezaei Hosseinabadi et al., 2014) proved that the intended functional  
250 groups are present on the full pore surface. In contrast, the reaction of the phosphonic acid groups  
251 with the surface of a native membrane occurs via condensation reactions with one or more OH-  
252 groups resulting in the formation of one or more oxygen bridging (-M-O-P-R) bonds. The complex  
253 bonding of phosphonic acid grafted groups has been shown in different papers (see e.g. the review  
254 of Meynen et al., 2014).

255 Modified membranes are denoted by a three-letter code: MGR are methyl grafted and PGR are  
256 phenyl grafted membranes by the Grignard grafting technique; MPA are methyl grafted  
257 membranes by the phosphonic acid grafting technique. As shown in our previous study, phenyl

258 grafted membranes by the phosphonic acid grafting technique (PPA) are too hydrophobic and  
259 therefore not used in this study (Mustafa et al., 2014).

260

## 261 **2.3. Characteristics of the feed solutions**

262 Fouling tests were performed by the filtration of model solutions or real wastewaters belonging to  
263 the three categories PPME, OOWW and PW. The characteristics of the three types of feed solutions  
264 are discussed in this section.

265

### 266 **2.3.1. Pulp and paper mill effluent (PPME model solution)**

267 PPME typically comprises a complex mixture of wood compounds (lignin, hemicelluloses, and  
268 others) and process chemicals (e.g. resin acids), which may have a polymeric, oligomeric, or  
269 monomeric nature. Model solutions mimicking the fouling tendency of PPME were prepared using  
270 a wood extract (WE), extracted at a high temperature. The WE was used to make model solutions  
271 by diluting it into pure water at a concentration of 1.1 and 2.2 g/L. Such solutions comprise wood  
272 hemicelluloses and lignins at wide molar mass ranges and a minor amount of wood lipophilic  
273 extractives. They have shown to create a high fouling tendency for many polymeric membranes  
274 (Ramamurthy et al., 1995). The general chemical structural formula of lignin and hemicellulose is  
275 shown in figure 1A.

276

277 Figure 1

278

### 279 **2.3.2. Olive oil wastewater (OOWW, real wastewater)**

280 In case of OOWW, real wastewater was used to investigate the membrane fouling. The provided  
281 real OOWW was dirty water, containing different soluble organic and inorganic ingredients,  
282 including insoluble sludge. The organic ingredients present in the provided OOWW most probably  
283 include extracellular polymeric substances (EPS) and several different polyphenols such as  
284 hydroxytyrosol, hydroxytyrosol 4-O-glucoside, Apigenin, 3, 4-dihydroxyphenyl glycol, tyrosol, and  
285 ferulic acids. Normally, these organic substances, especially the polyphenols (as they are higher in  
286 concentration in the provided OOWW), act as foulants during the membrane filtration. A general  
287 chemical structural formula of a typical polyphenol is shown in figure 1B.

288 For the filtrations at the DE set-up, real OOWW was used without any pretreatment, while for the  
289 filtration at the CF system, the wastewater was pre-treated, i.e. pre-filtered by a 200 µm filter. The  
290 pre-treatment was done because OOWW contained insoluble sludge, which could block the 200  
291 µm filter incorporated in the CF filtration unit.

292

### 293 **2.3.3. Oil/water emulsions (PW model solution)**

294 Two oil/water emulsions were prepared mimicking real oily wastewater from oil and gas  
295 production i.e. PW. They contain high salt concentrations next to 2400 ppm of oil and 240 ppm of  
296 surfactants. The content of the model oil/water emulsions are detailed in table 1. Emulsion 1 has  
297 negatively charged droplets due to the anionic surfactants (i.e. sodium dodecyl sulfate) and  
298 emulsion 2 has positively charged droplets because of the added cationic surfactants (i.e. benzyl-  
299 dimethyl-tetradecyl-ammonium chloride). All components of each emulsion were mixed together  
300 and ultrasound was applied to stabilize the emulsion. The exact procedure to make oil/water  
301 emulsions is briefly described as follows: pure water was taken in a glass beaker (e.g. 5 liter glass  
302 beaker), then we added 2400 mg/L hexadecane (model oil) and 240 mg/L of the surfactant and  
303 finally 10 g/L of sodium chloride. For emulsification and stabilization, ultrasound with an amplitude  
304 of 50% was applied for 30 min. For ultrasound, a sonifier 250 (Branson) apparatus was used.

305

306 Table 1. Prepared oil/water emulsions recipes.

Ingredients	Standard emulsion 1	Standard emulsion 2
Hexadecane	2400 ppm	2400 ppm
Sodium dodecyl sulfate	240 ppm	-
Benzyl-dimethyl-tetradecyl-ammonium chloride	-	240 ppm
Sodium chloride	10.000 ppm	10.000 ppm
Ultrasound, time (min)	30	30
Ultrasound, amplitude (%)	50	50

307

308 The surfactants lead to the formation of stable oil in water emulsions (“milky” aspect of the water),  
309 containing small oil droplets floating in the main water phase. The scheme of figure 1C shows that  
310 the surfactants surround the oil droplets, in such a way that the hydrophobic tail of the surfactant  
311 is immersed in the oil, while the charged head of the surfactant is positioned at the surface of the  
312 oil droplets, in contact with the polar water. The charged heads of the different surfactant  
313 molecules distribute themselves over the surface of the oil droplets. Hence, the nature of the head  
314 group is important as it might influence the fouling behavior in a different way. The chemical  
315 structure of the surfactant heads is shown as well.

316 The size of the oil droplets, measured by a Nanosight NS500 particle size analyzer, was in the range  
317 of 0.1 - 0.5  $\mu\text{m}$  with a volume average particle diameter of 0.3  $\mu\text{m}$ .

318

## 319 **2.4. Fouling measurements**

320 To assess the fouling, a specific filtration procedure was followed, as described elsewhere (Mustafa  
321 et al., 2016). A brief summary of the procedure is described as follows: Before every fouling  
322 measurement, an initial pure water flux (stable flux after 1 hour denoted as " $J_0$ ") was measured in  
323 cross-flow (CF). Then, fouling was induced by the filtration of the real wastewater or model  
324 wastewater solution, in dead-end (DE) or in CF mode. At DE, the filtration of the foulant solution  
325 was performed until one liter of the two liter feed was permeated, while the CF filtration was  
326 performed for ~24 hrs. In this study, longer filtration did not further decrease the flux (increase the  
327 fouling) significantly. Finally, again the CF pure water flux (stable flux after 1-2 hours denoted as  
328 " $J$ ") was determined. This CF water filtration also acts as forward flushing and removes the  
329 reversible part of the fouling (Mustafa et al., 2016). The antifouling/fouling tendency of the  
330 membranes was eventually evaluated by calculating the normalized flux decline i.e. " $J/J_0$ ".

331 All foulant filtrations were performed at ambient temperature (i.e. 25 °C), with cross-flow velocity  
332 2 m/s (in case of CF filtration) and the applied trans membrane pressure (TMP) was 1 bar for UF  
333 and 5 bar for NF. All water filtrations were performed at TMP 5 bar. To avoid confusion, the  
334 evolution of the normalized fluxes calculated from filtration results obtained in the CF set-up are  
335 always represented with solid lines, and dotted lines represent normalized fluxes after DE filtration.

336

## 337 **2.5. Membrane characterization and sample analysis**

338 All membranes (grafted and native TiO<sub>2</sub> membranes) were characterized for their pure water flux  
339 ( $J_0$ ) before fouling. For NF membranes, all characteristics of the grafted and native membranes such  
340 as molecular weight cut-off (MWCO), water contact angle (CA) and pure water flux are similar as in  
341 (Mustafa et al., 2016) and repeated here for convenience All results are summarized in table 2. It  
342 can be observed that the obtained MWCO values are all very similar, indicating that the pore size  
343 did not change significantly by the grafting, as already noticed in (Mustafa et al., 2014, 2016).

344

345 Table 2. The obtained MWCO (Da), CA (°) and pure water flux (L/hm<sup>2</sup> bar) values of all investigated NF (0.9 nm) TiO<sub>2</sub>  
346 membranes, and pure water flux values of all investigated UF (30 nm) membranes. The given ranges show the variability  
347 of the values when measured on different membrane specimens of the same membrane type.

348

349

Membrane ID	UF membranes	NF membranes		
	water flux (L/hm <sup>2</sup> bar)	water flux (L/hm <sup>2</sup> bar)	MWCO (Da)	CA (°)
Native	170-200	10-30	450-550	10-20
MGR	104	5-13	450-550	50-60
PGR	-	5-14	450-550	50-60
MPA	118	8-27	450-550	35-45

350

351 The contact angle results show that the grafting with methyl and phenyl groups logically decreased  
 352 somewhat the hydrophilicity of the membranes. Correlated, the water flux of the MGR membrane  
 353 is roughly about 50% of that of the native membrane, the flux of the MPA membrane is more than  
 354 60% of that of the native membrane. The grafted membranes are not fully hydrophobic, but can  
 355 be considered as amphiphilic.

356 The concentration of organic materials in permeates and retentates have been determined by UV  
 357 absorbance at 254 nm (UV1800 Shimadzu UV spectrophotometer CPS Tem. Controller), probing the  
 358 aromatics in the organics. Chemical oxygen demand (COD) was determined by a UV spectrometer  
 359 (AvaSpec-2048-2) and total organic carbon (TOC) was measured by a catalytic high temperature  
 360 combustion instrument with selective detection of CO<sub>2</sub> (Multi N/C 2100, Analytik Jena, Jena,  
 361 Germany). Hexadecane was determined by gas chromatography equipped with a flame ionization  
 362 detector (GC-FID): Column DB-5MS 15 m with a 0.25 mm internal diameter and 0.25 μm film  
 363 thickness, calibration solutions of n-C16 in n-C6 (range 1-1000 μg/g) were applied.

364 With the help of the concentration values in permeates, retentates and feed, retentions were  
 365 calculated by the following equation:

366

$$367 \text{ Retentions (\%)} = 100 \{ \text{Log (Cr/Cf)} / \text{Log VCF} \} \approx 100 (1 - \text{Cp/Cr})$$

368

369 Where Cr = concentration in retentate, Cp = concentration in permeate, Cf = concentration in feed,  
 370 and VCF = Volume concentration factor. The VCF in the filtration experiments was 2 at the  
 371 maximum.

372

## 373 2.6. Chemical cleaning

374 Usually, after fouling, membranes are recovered by chemical cleaning using different chemicals  
375 depending upon the nature of the fouling and the foulants. The chemical cleaning procedure and  
376 choice of cleaning agents are detailed elsewhere [Mustafa et al., 2016].

377 In this study, the membranes fouled by PPME model solutions and by OOWW were cleaned by  
378 using alkaline cleaning agents such as P3 Ultrasil 110 (upto pH 12). In case of oil/water emulsions,  
379 besides alkaline cleaning agents, acidic cleaning agents such as P3 Ultrasil 75 and sulfuric acid were  
380 also used with different concentrations depending upon the fouling severity (upto pH 2).

381 After each chemical cleaning, rinsing with pure water was done, and subsequently the pure water  
382 permeability was determined to estimate the cleaning efficiency.

383

### 384 **3. Results**

385 The antifouling behavior of the grafted membranes compared to the native membranes was  
386 investigated for the three difficult wastewater streams using the procedure described above. In the  
387 following, all obtained results relevant to the three-wastewater streams will be described  
388 separately before the discussion.

389

#### 390 **3.1. Pulp and paper mill effluents**

391 Figure 2 shows the irreversible fouling (normalized flux decline) of all grafted and native NF  
392 membranes during the filtration of two model solutions with different concentrations (i.e. 1.1 g or  
393 2.2 g of WE in one liter of water) in the DE set-up.

394

395 Figure 2

396

397 Overall, the results of the fouling experiments with the PPME model solutions confirmed the  
398 positive effect of the grafting on the fouling behavior. The MGR and PGR membranes both show a  
399 remarkable antifouling behavior, whereas the fouling of the MPA membranes is also clearly  
400 diminished compared to the native membrane, which is fouled maximum in both cases. This trend  
401 of membrane fouling is similar to the fouling results that were already reported for other foulants  
402 in our previous study (Mustafa et al., 2016, fouling with natural organic matter). In case of the  
403 higher concentration (i.e. 2.2 g/L) of the WE model foulant, the irreversible fouling of all  
404 investigated membranes is somewhat higher. This may be due to layer by layer fouling (Mustafa et  
405 al. 2014).

406 We performed the measurements in DE mode to maximize foulant-membrane interactions.  
407 However, for real applications, NF will be normally performed in cross flow mode. Therefore, we

408 also did filtration of a model solution (containing 2 g WE per liter of water) in a CF system for about  
 409 24 hrs. This filtration was only performed through MGR (best performing membranes) and native  
 410 membranes for comparison. The membranes used were the fully recovered, chemically cleaned  
 411 membranes after the dead end fouling. The flux decline profile of both MGR and native  
 412 membranes in this CF fouling, is shown in figure 3 (left).

413

414 Figure 3

415

416 Again, the trend of the flux decline for both MGR and native membranes make it obvious that MGR  
 417 has significant antifouling behavior. Indeed, the flux declined from 45 to 27 L/hm<sup>2</sup> in 24 hours for  
 418 the MGR membrane (i.e.~40%) as compared to the native membrane where the flux declined much  
 419 more from 60 to 17 L/hm<sup>2</sup> in 24 hours (i.e.~73%).

420 Moreover, from figure 3 left, it is also clear that the process flux is more stable and the highest for  
 421 the MGR membrane, even though the pure water flux of this membrane is more or less 50% lower  
 422 than that of the native membrane (table 2). After the CF filtration of the model solution, a pure  
 423 water filtration was performed in CF, to remove the reversible part of the fouling by forward  
 424 flushing. The remaining part of the fouling after forward flushing was evaluated by calculating the  
 425 normalized flux " $J/J_0$ ", and is shown in figure 3 (right), representing the irreversible fouling. The  
 426 obtained results show that not only the flux decline of the native membrane was higher during the  
 427 CF filtration of this WE model foulant solution: also, the irreversible fouling is much higher (73% for  
 428 the native membrane and only 13% for the MGR membrane). It is worth to mention that the entire  
 429 flux decline observed during the 24 hours CF filtration, in case of the native membrane, is caused  
 430 by irreversible fouling, while in case of the MGR membrane, a significant part of the flux decline  
 431 during the filtration is reversible by forward flushing. Hence, the flux decline is not only less in case  
 432 of MGR, also its operability allows a much longer use due to the option of physical cleaning in  
 433 contrast to the native membrane.

434

435 Table 3. TOC retentions through the grafted and the native membranes during the filtration of the PPME model solutions  
 436 both in DE and CF systems.

Membrane	TOC Retentions (%)	
	DE filtration (2.2 g/L)	CF filtration (2.0 g/L)
Native	86	94
MPA	90	-
MGR	91	96

437

438 We also measured permeate water quality through the investigated membranes both during DE  
439 and CF filtration of the WE model foulant solutions. The TOC retentions are given in table 3. The  
440 retention values are quite high and comparable for all investigated grafted and native membranes.  
441 These high and similar retentions are quite normal because the molecular size of organic polymers  
442 such as lignins and/or hemicellulose etc., present in wood extract, is far higher than the pore size of  
443 the investigated NF membranes, and grafting did not change the pore size of the membranes  
444 (Mustafa et al., 2014; 2016). However, the TOC retention values for all the membranes during the  
445 DE filtration are somewhat less as compared to the retentions for the same membranes during the  
446 filtration in CF. This may be due to the higher concentration polarization at DE filtration compared  
447 to the CF filtration (further discussed in section 4).

448 As mentioned earlier, chemical cleaning was done after the membrane fouling. The chemical  
449 cleaning recovered the water flux to its original value. For the native membrane, chemical cleaning  
450 at higher pH (i.e. pH 12) was required, while all grafted membranes were fully recovered at lower  
451 pH (i.e. pH 10). In many cases, the MGR membrane recovered by exposing the membrane just to  
452 pure water at room temperature (forward flushing). These cleaning results also show indirectly the  
453 difference in interaction strength between the foulants and the membranes and confirm the  
454 fouling results. All results will be discussed in detail in section 4.

455

### 456 **3.2. Olive oil wastewater**

457 In all our previous studies (Mustafa et al., 2014; 2016) and again here in the PPME experiments, the  
458 MGR membrane has the best antifouling tendency among the grafted membranes. Therefore, we  
459 decided to do filtration of OOWW only through the MGR and native NF membranes.

460 Similar to PPME model solutions, we first performed filtration of the real OOWW in the DE set-up  
461 to provide maximum chances to the foulants, present in OOWW, to foul the membranes. The  
462 normalized flux decline (figure 4) clearly shows that the native membrane is fouled about 60%,  
463 while the MGR membrane was not irreversibly fouled.

464

465 Figure 4

466

467 After filtration of the OOWW in the DE set-up, we also performed a longer-term (more than 24  
468 hours) filtration of the OOWW in CF mode (pre-filtration over a 200  $\mu\text{m}$  filter was performed to  
469 protect the installation). To rule out the effect of flux on the fouling (Mustafa et al., 2016), we

470 choose 2 new native membranes: one with about the same pure water flux as the MGR membrane  
471 (i.e. 70 L/hm<sup>2</sup> at 5 bar TMP), and one with a somewhat higher flux i.e. 85 L/hm<sup>2</sup> at 5 bar TMP. The  
472 MGR membrane of the DE test was used directly in the CF test, without cleaning, as the membrane  
473 was not fouled (see figure 4).

474

475 Figure 5

476

477 Figure 5 shows the flux evolution of MGR and the native membranes during filtration of real  
478 OOWW for about 24 hours filtration in CF system. For the native membranes, the permeate flux  
479 rapidly decreased during the first hour, reaching a steady-state value of about 7-10 L/hm<sup>2</sup>. In  
480 comparison, the MGR membrane flux decreased, but not sharply as in the case of the native  
481 membranes, and reached a steady-state value of about ~28 L/hm<sup>2</sup>. The flux decline difference is  
482 again clearly showing that the grafting is significantly enhancing the antifouling tendency of the  
483 TiO<sub>2</sub> NF membrane, leading to a significant increase of the process flux. Note that the starting pure  
484 water flux of the native membranes has little influence on the stable process flux after 24 hours:  
485 only the flux decrease at the start of the filtration is stronger. Remark also that the ratio of the pure  
486 water flux to the stable process flux is less than 3 for MGR while more than 8 for the native  
487 membranes.

488 The native permeate flux profiles show an initial sharp drop followed by a smoother but continuous  
489 flux drop until a steady state is reached (7-10 L/hm<sup>2</sup>). This kind of profile can be caused by both  
490 concentration polarization and/or cake layer formation (mostly reversible) and irreversible fouling.  
491 To investigate this, forward flushing of all the membranes after the OOWW filtration in CF was  
492 performed by applying pure water filtration using constant parameters (5 bar TMP, 2 m/s flow  
493 velocity, and feed temperature ~25 °C) until a stable pure water flux was acquired. The obtained  
494 results were very similar to DE filtration results (figure 4), the MGR membranes were recovered  
495 100% by only forward flushing of pure water (0% irreversible fouling), while native membranes  
496 recovered only less than 45% (native membrane fouled more than 55% irreversibly).

497 As usual, all OOWW fouled native membranes were recovered completely after chemical cleaning  
498 by using a P3 Ultrasil 110 solution of pH 12.

499 The water quality of the produced permeates after the filtration of OOWW in CF was estimated by  
500 measuring pH, conductivity, and chemical oxygen demand (COD). The obtained values of the feed  
501 and the permeates are given in table 4. The results show that the water quality after OOWW  
502 filtration through the MGR membrane is far better than through the native membrane, as COD of  
503 the OOWW decreased to 48% by the MGR membrane while only to 11% by the native membrane.

504 So grafting did not only significantly enhance the antifouling tendency (both reversible and  
 505 irreversible) of TiO<sub>2</sub> NF membranes, but also improved the permeate water quality. The obtained  
 506 COD retentions through the MGR membrane are higher than the native membrane, most probably  
 507 due to a smaller (reversible) fouling layer on this membrane (during CF filtration). This will be  
 508 discussed in detail in section 4.

509

510 Table 4. Permeate water quality of both MGR and native membranes after the filtration of OOWW in CF mode (feed was  
 511 real OOWW after 200 μm pre-filtration).

Membrane id	pH permeate/feed	Conductivity (mS/cm) permeate/feed	COD (mg/l) Permeate/feed	COD Retentions (%)
MGR	3.8/4.7	3.2/4.5	12.1/23.3	48.0
Native	3.5/4.7	4.9/4.5	20.9/23.3	11.0

512

### 513 3.3. Model oil/water emulsions

514 In contrast to all previous filtrations or fouling measurements, filtration of oil/water emulsions  
 515 were performed using native and grafted UF membranes with an average pore size of 30 nm.

516 Three open membranes, namely native, MGR and MPA (pure water flux values in table 2), were  
 517 subjected to the filtration of the two self-prepared model oil/water emulsions, mimicking PW. The  
 518 procedure to measure or induce the fouling was similar to the procedure that was adopted in case  
 519 of NF membranes. The only difference is that all the filtrations were now performed at 1 bar TMP,  
 520 while in case of the NF membranes, all filtrations were performed at 5 bar TMP.

521 The normalized flux decline of all three membranes (native, MGR and MPA membranes) after  
 522 filtrations of both emulsions in DE set up is shown in figure 6. The trend of obtained normalized flux  
 523 decline of all investigated open (UF) membranes by model oil/water emulsions is quite similar to  
 524 the obtained flux decline of the NF membranes after the filtrations of real OOWW and model  
 525 solutions mimicking PPME. The grafted membranes (both MPA and MGR membranes) fouled less  
 526 than the native membranes, and especially the MGR membrane fouled again very low by both  
 527 emulsions. Remark that in this wastewater the MPA membrane shows also relatively low fouling.  
 528 The MGR membrane fouled less than 10% while the native membrane fouled more than 50% after  
 529 the filtrations of both oil/water emulsions.

530

531 Figure 6

532

533 Similar to the other two waste streams (OOWW and PPME) in this study, filtration of both oil/water  
534 emulsions was also performed in CF through all investigated types of membranes (after proper  
535 cleaning). Filtration of both oil/water emulsions in CF mode was performed for 24 hours under 2  
536 m/s flow velocity, 1 bar TMP, and feed temperature was 23-25 °C. The observed flux decline of all  
537 investigated membranes by both emulsions is shown in figure 7.

538

539 Figure 7

540

541 Figure 7 shows that during the CF filtration of oil/water emulsions, the process flux decreased  
542 about 50% in case of the native membrane for both emulsions while the flux of the MGR and MPA  
543 membrane remained more or less constant. Only a slight decrease, especially in case of emulsion 2,  
544 can be observed. Moreover, the flux of the MGR and MPA membrane becomes higher than the  
545 native membrane just after 1-2 hours of filtration of both oil/water emulsions, although the  
546 starting flux of the MGR and MPA membrane was lower than the native membrane in each case.  
547 The process flux of the MPA membrane, starting at a slightly higher value, also decreased, but less  
548 than the native membrane and more than the MGR membrane, showing intermediate behaviour  
549 as seen before (Mustafa et al., 2014; Mustafa et al., 2016).

550 Similar to the other two wastewater streams, forward flushing by pure water on all the membranes  
551 was also performed after the filtration of both emulsions in CF mode. The obtained results  
552 (normalized flux values) are shown in figure 8.

553 It is obvious from figure 8 that the MGR membrane is not irreversibly fouled in case of emulsion 1  
554 (in contrast to DE filtration where MGR membrane was slightly fouled), and only mildly fouled by  
555 the filtration of emulsion 2 (somewhat similar to DE filtration). In comparison, the native  
556 membrane irreversibly fouled more or less 40% in case of both oil/water emulsions. Again, the  
557 irreversible fouling of the MPA membrane is in-between of the MGR and the native membrane for  
558 both emulsions.

559 It is important to mention that all grafted and native membranes were chemically cleaned in-  
560 between the filtrations of emulsions using different acidic and basic cleaning reagents. Grafted  
561 membranes were recovered after chemical cleaning using alkaline cleaning solutions at pH 10 and  
562 acidic solution at pH 3, while native membranes were recovered at pH 12, and then pH 2.  
563 Sometimes, native membranes were not recovered completely under the applied conditions (i.e  
564 pH 2-12), in that case a new native membrane was used for next measurements.

565 Thus, on the basis of these experimentally obtained results, it is clear that our antifouling grafting  
566 is not only applicable on NF membranes (0.9 nm pore size) for drinking water production (Mustafa

567 et al., 2014; Mustafa et al., 2016) and wastewater treatment (previous sections of this study), but  
568 also on open (UF) membranes (30 nm pore size) for the treatment of PW.

569

570 Figure 8

571

572 Similar to the other two waste streams, we measured retentions of oil (hexadecane) by all three  
573 investigated membranes during the filtrations of oil/water emulsions in both DE and CF modes. The  
574 obtained results are shown in table 5. The obtained oil retentions by both types of grafted  
575 membranes are very high and comparable with those of the native membrane. The obtained oil  
576 retention values confirm that the permeate water is reusable without any further treatment after  
577 the filtration of the model PW by the investigated membranes (limit aimed for in the oil industry is  
578 <30 ppm oil) (OSPAR convention in Valencia, 2001). All obtained results will be discussed in detail in  
579 section 4.

580

581 Table 5. The obtained oil (hexadecane) retentions by the investigated membranes during the filtration in both CF and DE  
582 modes.

Membr. Id	<u>Hexadecane retentions (%)</u>			
	DE filtration		CF filtration	
	Emulsion 1	Emulsion 2	Emulsion 1	Emulsion 2
<b>Native</b>	99.9	99.9	99.9	100
<b>MPA</b>	99.8	99.9	99.9	99.9
<b>MGR</b>	100	99.9	100	100

583

584

## 585 4. Discussion

586 All experimentally obtained results of fouling using the three difficult wastewater streams (i.e.  
587 model solutions mimicking PPME, real OOWW and model oil/water emulsions mimicking PW) can  
588 be explained similar to the humic acid fouling results that were elucidated in our previous studies  
589 (Mustafa et al., 2014; 2016). The explanation takes into account the physico-chemical properties of  
590 foulants and membranes and their interactions. Similar to humic acids, all foulants present in the  
591 feed solutions used here contain mainly polar functional groups (such as OH and COOH, figure 1A  
592 and 1B) or charged groups (such as  $-\text{SO}_3^-$ ,  $(\text{R})_4\text{N}^+$  on the surface of the oil droplets, figure 1C), as  
593 explained in section 2.3, These groups cause strong polar and/or electrostatic interactions with the  
594 hydrophilic native membranes (plenty of surface OH groups). Therefore, native membranes foul

595 much more than all other investigated membranes throughout the measurements in this study.  
596 Similarly, polar interactions are also possible in case of MPA membranes but less than the native  
597 membranes because of the reduced number of OH groups, and the steric hindrance of the grafted  
598 functional group (Mustafa et al., 2014; 2016).

599 In case of PPME model solution, the PGR membrane also fouled, although much less than the MPA  
600 and the native membranes. This is most likely because of the presence of some  $\pi$ - $\pi$  interactions  
601 between the PGR membrane and the foulants (i.e. lignin see figure 1A) present in the used model  
602 solutions (Mustafa et al., 2014; 2016). However, the fouling degree of the PGR membrane in this  
603 case is far less than the PGR membrane fouling by humic acid (HAs) solutions (Mustafa et al., 2014;  
604 2016). This is quite logical because the aromaticity of the WE solution is far less as compared to  
605 HAs (UV absorbance at 254 nm is 0.27 for a 10 mg/L HAs solution, while only 0.02 for a WE solution  
606 of the same concentration), leading to less  $\pi$ - $\pi$  interactions. For comparison, the PGR was fouled  
607 ~50% in case of HAs (Mustafa et al., 2014) and fouled ~10% in the present case, which is in  
608 accordance to the aromaticity present in both type of the foulants. Of course, the correlation is not  
609 linear as the fouling is determined by the whole of aromaticity, polar and other types of  
610 interactions, which is different in case of HAs and WE.

611 It is important to notice that, the MGR membrane showed again no to very mild fouling (as for  
612 HAs). All filtrations, with all three different foulant streams, both in DE and in CF, made it clear that  
613 the MGR grafting prevented the membranes from severe irreversible fouling, which occurred with  
614 the native membranes. Moreover, in all the cases, during the filtration at CF, the process flux or  
615 filtration capacity of the MGR membranes is higher as compared to the native membranes, even  
616 though the pure water flux of the MGR membranes was less than that of the native membranes.  
617 This can be explained again by the absence of any strong interactions between the MGR membrane  
618 and the polar/charged groups of the foulants, as in previous work (Mustafa et al., 2014, 2016).  
619 Consequently, the flux also remains relatively constant over time. Hence, the strong anti-fouling  
620 behavior of the MGR membrane is repeatedly proven, and the inert character of the MGR  
621 membrane is confirmed.

622 In addition, the chemical cleaning efficiency also shows indirectly that the foulants have stronger  
623 interactions towards the native and much weaker interactions towards the MGR membranes.  
624 Chemical cleaning recovered the flux to the original value in both the grafted and the native  
625 membranes, but native membranes only recovered at a higher pH of the cleaning solution (i.e. pH  
626 2-12), while all the grafted membranes were recovered at lower pH (i.e. pH 3-10). In some cases,  
627 the MGR membrane recovered even by exposing the membrane just to pure water at room  
628 temperature (i.e. forward flush), while sometimes native membranes did not recover completely

629 especially after fouling by model oil/water emulsions, even not by harsh cleaning solutions (i.e. pH  
630 2-12). Remark that the grafted membranes are sufficiently stable under all mentioned conditions  
631 (pH 2 – 10).

632 From our previous research it is known that the grafting did not change the cut-off and thus the  
633 rejection ability (similar molecular weight cut-off values, see Mustafa et al. 2014) of the  
634 membranes significantly. This is confirmed here in case of model solutions mimicking PPME and  
635 PW. We remark that the very high retentions of the oil (hexadecane) in water emulsions over the  
636 30 nm membranes, is most likely due to size exclusion. As mentioned in section 2.3.3, the average  
637 droplet size of the used model emulsions is about 0.3  $\mu\text{m}$ , which is far higher than the 30 nm pore  
638 size of the investigated UF membranes.

639 However, it is well known that membrane fouling not only reduces the permeate flux but can also  
640 change membrane selectivity and/or rejections (Belfort et al., 1994; Tarleton Wakeman, 1993). This  
641 could be the case for the OOWW stream in this study. The presence of interactions between the  
642 foulants/contaminants (e.g. polyphenols in this case) and the membrane surface could indirectly be  
643 responsible. For example, in case of native membrane, the interactions between the membrane  
644 surface and foulants (i.e. polyphenols etc.) are stronger, resulting in an accumulation of the  
645 foulants at the surface or in the pores of the membrane, consequently the membrane feels a  
646 higher concentration of foulants as compared to the MGR membrane, which could lead to the  
647 lower retentions of these membranes. Similar concentration polarisation effects can explain also  
648 the somewhat higher retentions in the DE filtrations compared to the CF filtrations.

649 Similar to our previous study (Mustafa et al., 2014; 2016) and as indicated by Whiteside and others  
650 (Holmlin et al., 2001; Ostuni et al., 2001) for other applications, it is clear that high hydrophilicity as  
651 such is not the trigger for lower fouling (as often noted in literature on polymeric membranes). A  
652 grafted membrane surface with amphiphilic properties, especially when steric effects limit direct  
653 contact of the foulant to the reactive functional groups on the surface of the membrane (e.g. in  
654 case of MGR), performs much better than the membrane surface that is strictly hydrophilic (as the  
655 native membranes). Zhu and co-workers (Zhu et al., 2013) reported more or less similar type of  
656 results for oil in water emulsions with polymeric membranes. They found that a membrane surface  
657 having both hydrophilic and oleophobic properties performed better than a membrane surface  
658 that was more hydrophilic, especially during the filtration of PW. Moreover, also the influence of  
659 steric effects was acknowledged. This study confirms these results as the MGR membranes with  
660 amphiphilic properties performed best among the investigated membranes. Such an amphiphilic  
661 surface, is relatively “inert” towards adsorption of foulants, and at the same time has still enough  
662 affinity for water.

663 Finally, the similarities in the performance of the MGR grafted membranes in the different  
664 wastewater streams, independent of their composition, clearly indicate the generic nature and  
665 broad applicability of MGR grafted membranes in a wide variety of different wastewater streams.  
666 This shows their high potential to overcome the mentioned drawbacks in the state of the art such  
667 as complex, variable and sometimes unknown compositions over time that limit applicability with  
668 other methods or membranes. Moreover, their high retentions and also their economic and stable  
669 process flux has been shown beneficial in the various wastewater treatments.

670

## 671 **5. Conclusion**

672 The results obtained during filtration of three challenging wastewater streams, confirm the strong  
673 antifouling effect of grafting seen before for surface/ground water foulants. Again, the MGR  
674 membrane was not fouled, or only mild fouled in case of high concentration of foulants. All  
675 filtrations, both in DE and in CF modes, made it clear that the MGR antifouling grafting prevented  
676 the membranes from severe irreversible fouling, which occurred with the native membranes.  
677 Moreover, in all these cases, during the filtration in CF mode, the process flux or filtration capacity  
678 of MGR membranes (and MPA membranes in case of PW) is more stable and higher as compared  
679 to the native membranes, although the pure water flux of the MGR (and MPA) membrane was in  
680 most cases only about half of that of the native membrane. Hence, it is repeatedly proven that only  
681 limited/weak interactions are possible between the MGR membrane and the severe foulants found  
682 in the tested wastewaters. Hereby, the inert character of the MGR membrane is confirmed in a  
683 broad variety of fouling situations. This study has also shown that similar antifouling effects can be  
684 realized for UF as for NF membranes.

685 The permeate quality through all grafted membranes is quite comparable with the native  
686 membranes especially in case of PPME and PW. In case of OOWW, even higher rejection of COD is  
687 observed by the MGR membrane as a consequence of the lower fouling. So for OOWW, MGR  
688 grafting enhances the overall membrane performance by minimizing the fouling tendency, keeping  
689 much higher and more stable process flux, and improving the produced permeate water quality as  
690 well.

691 As in previous studies, it is clear that high hydrophilicity as such is not the trigger for lower fouling  
692 (as often noted in literature on polymeric membranes) but rather the absence of direct and/or  
693 strong contact of foulants to the reactive functional groups on the surface of the membrane.

694 In short, the MGR antifouling grafting of ceramic membranes was validated in a variety of difficult  
695 wastewaters, and the MGR membrane could provide a good economical solution for the treatment  
696 of the selected challenging wastewater streams.

697

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705

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