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1 **New insights into the fouling mechanism of dissolved**
2 **organic matter applying nanofiltration membranes**
3 **with a variety of surface chemistries**
4

5 **Ghulam Mustafa^{†‡}, Kenny Wyns[‡], Anita Buekenhoudt^{*‡}, and Vera Meynen^{†‡}**

6 [‡]VITO NV - Flemish Institute for Technological Research NV, Boeretang 200, B-2400 Mol, Belgium,
7 Tel.: +32 14 335790

8 ^{*}Laboratory of Adsorption and Catalysis (LADCA), Department of Chemistry, University of Antwerp, CDE,
9 Universiteitsplein 1, B-2610 Wilrijk, Belgium, Tel.: +32 3 2652368

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11 E-mail: anita.buekenhoudt@vito.be
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27 **Abstract**

28 Nanofiltration (NF) membrane fouling by DOM remains a major and poorly understood
29 issue. To acquire a better insight we studied the fouling of the DOM fractions humic acids
30 (HAs) and fulvic acids (FAs), with and without Ca^{2+} , on native and grafted ceramic NF
31 membranes. Grafting with two methods and three different grafting groups allowed to
32 create a range of membranes with a variety of surface chemistries, and a wide range of
33 surface polarity, much broader than ever used in previous studies. A typical polymer
34 (polyamide) NF membrane was included for comparison. All obtained results reveal that
35 membrane fouling is not determined by membrane hydrophilicity/ hydrophobicity as a
36 general and sole criterion, but rather on the whole of the surface chemistry determining the
37 amount and strength of the possible foulant-membrane interactions. As a consequence the
38 effect of inorganic ions on the fouling is also dependent on the surface chemistry. Important
39 new insights in the DOM fouling mechanism was acquired, shedding new light on the state-
40 of-the-art knowledge.

41

42

43 **Keywords**

- 44 • Nanofiltration
- 45 • Water treatment
- 46 • Membrane fouling
- 47 • Fouling mechanism
- 48 • DOM fractions
- 49 • Inorganic ions

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55 **1. Introduction**

56 With the increasing demand for **clean and fresh water**, many new technologies of water
57 purification are being developed. Since the last two decades, membrane technology has
58 emerged as a worthwhile treatment to comply with existing and pending water quality
59 regulations (Singh 1998; Wiesner and Chellam, 1999; Meng et al., 2009; Guo et al., 2010;
60 Hwang et al., 2010; Diagne et al., 2012; Freeman and Shorney-Darby, 2011). Currently,
61 particular interest has been raised in the use of **nanofiltration (NF)** as a single-step
62 treatment alternative, offering a resourceful approach to meet multiple water quality
63 objectives such as control of organics, inorganics and micro pollutants via a combination of
64 charge interaction and size exclusion (Eriksson, 1998; Hilala et al., 2004; Lerch and Lee, 2004;
65 Panglisch and Gimbel, 2005; Han et al., 2013). In addition, specific attention increases for
66 ceramic NF membranes combining robustness with high water flux due to its high
67 hydrophilicity.

68 However, **fouling** is still a major and poorly resolved problem in all membrane-based
69 separation processes especially for water treatment (Chang et al., 2002; Goosen et al., 2004;
70 Drews, 2010; Ni et al., 2011, Ajmani et al., 2012). Prosperous and effective applications of
71 membrane technology has been critically limited and hampered by membrane fouling.
72 Membrane fouling is attributed to the physicochemical interactions between the impurities
73 present in the feed, and the membrane surface. Therefore, fouling of membranes and
74 especially NF membranes, depends on many parameters such as membrane material,
75 surface roughness (Elimelech et al., 1997), surface chemistry, porosity, operational
76 conditions, and of course feed water quality (Nyström et al., 1995). Fouling, associated with
77 accumulation of substances on the membrane surface or within the membrane pores by
78 charge or other strong interactions, is known as **irreversible fouling** (or chemical fouling) and
79 can only be removed by chemical cleaning (Clark et al., 1991; Su et al., 2000; Sun et al.,
80 2013).

81 A wide spectrum of ingredients or impurities in water contributes to irreversible fouling.
82 These include **dissolved organic matter (DOM)**, soluble inorganic compounds, and microbes.
83 DOM forms a major organic constituent in water especially in surface and ground water, and
84 it has been considered to be a significant foulant (Hong and Elimelech, 1997; Maartens et al.,
85 1998; Yuan and Zydney, 1999, 2000; Manttari et al., 2000). The role of DOM in fouling of

86 membranes has been pointed out by a number of investigators (Howe and Clark, 2002; Lee
87 et al., 2006; Huang et al., 2007; Katsoufidou et al., 2010; Zularisam et al., 2011; Aryanti et al.,
88 2015). Many researchers came to the conclusion that irreversible fouling is stronger for
89 more hydrophobic membranes, than for more hydrophilic membranes (Kulovaara et al.,
90 1999; Ma et al., 2001; Mohammadi et al., 2002) Furthermore, it has been abundantly shown
91 that membrane fouling by DOM is significantly enhanced in the presence of **divalent cations**
92 **(e.g. Ca²⁺)** (Jucker and Clark, 1994; Nystrom et al., 1996; Hong and Elimelich, 1997; Yuan and
93 Zydney, 2000; Tao et al., 2015).

94 Different aspects of DOM are important for its fouling behavior: charge, size and polarity.
95 Primarily, several researchers focused on fouling instigated by humic acids (HAs) and
96 ascribed it to hydrophobic interactions (Krasner et al., 1996; Nabe et al., 1997; Kulovaara et
97 al., 1999; Yuan and Zydney, 1999; Ma et al., 2001; Mohammadi et al., 2002; Giasuddin et al.,
98 2007; Lee et al., 2004; Costa et al., 2006; Yamamura et al., 2007; Katsoufidou et al., 2008;
99 Aryanti et al., 2015). HAs are larger size molecules rich in aromatic carbon, but having also
100 polar groups such as carboxylic and phenolic groups. During the last few years, membrane
101 fouling by the hydrophilic part of DOM, known as fulvic acids, was also considered
102 comprehensively (Kimura et al., 2004; Tian et al., 2013). Fulvic acids (FAs) are typically
103 smaller in size, having less aromatic carbon but relatively more polar functional groups.
104 Unfortunately, despite all these investigations, DOM membrane fouling has continued to be
105 a poorly understood phenomenon, as no clear understanding of DOM fouling could be
106 acquired hitherto (Huang, et al., 2007; Jermann et al., 2007; Katsoufidou et al., 2010;
107 Zularisam et al., 2011; Tian et al., 2013). Additionally, we want to stress that the majority of
108 these studies have been performed on polymeric membranes. To the best of our knowledge,
109 a detailed DOM fouling study on ceramic NF membranes has not been reported elsewhere.

110 In this paper, we were able to acquire important new insights into the fouling mechanism of
111 DOM, and in specific the role of ions (Ca²⁺). This was obtained by determining HAs and FAs
112 fouling with and without Ca²⁺ on ceramic (TiO₂) NF membranes with a wide variety of
113 surface chemistries. This is a unique approach, allowing to study DOM fouling for a broad
114 range of surface polarities, much broader than in any previous studies. To vary the surface
115 chemistries, two types of surface modifications were used: phosphonic acid grafting (Randon
116 et al., 1995; Mutin et al., 2005) and a recently developed innovative method based on
117 **Grignard chemistry** (Meynen et al., 2009; Rezaei Hosseinabadia et al., 2014; Mustafa et al.,

118 [2014](#)). For comparison also a commercially available polymeric (polyamide) NF membrane
119 was included in the study.

120 We want to stress that this is also the first systematic study with focus on understanding the
121 impact of inorganic ions on DOM fouling of ceramic membranes (particularly TiO₂ NF
122 membranes).

123

124 **2. Materials and Methods**

125 **2.1. Membranes and chemicals**

126 Commercially available, small-scale tubular (monochannel tubes having an outer diameter of
127 1 cm, and an inner diameter of 0.7 cm) TiO₂ NF membranes (denoted Native), with an
128 average pore diameter 0.9 nm were acquired from the company Inopor GmbH. The
129 molecular weight cut-off (MWCO) communicated by the supplier is 450 Da, characteristic for
130 NF membranes (200 < MWCO < 1000 Da). Flat sheet, thin film composite polyamide NF
131 membranes (denoted PolyA) having a backing material of polyester, and a total membrane
132 thickness of 0.0065 inches (0.165 mm) were provided by Synder Filtration. The MWCO as
133 communicated by the supplier is 600 Da, again in the correct range for NF membranes. All
134 necessary chemicals such as methyl phosphonic acid, methyl magnesium bromide, propyl
135 magnesium bromide, phenyl magnesium bromide, calcium chloride, and humic acids (HAs)
136 were purchased from Sigma Aldrich chemical company. Fulvic acids (FAs) was purchased
137 from a company named Wuhan Shengtong Jinde Chemical Co., Ltd, China. The alkaline
138 cleaning agent P3 Ultrasil 110 was delivered by Ecolab manufacturers. Pure water (reverse
139 osmosis quality water) with a conductivity of less than 15 µs/cm and pH 6.5 - 7 was used for
140 all filtration experiments and as a solvent for phosphonic acids graftings.

141

142 **2.2. Grafting of TiO₂ NF membranes**

143 Native TiO₂ NF membranes are highly hydrophilic membranes, containing abundant -OH
144 groups on their complete pore surface. To vary the surface chemistry of these membranes,
145 different native membranes were grafted using two different chemical modification agents:
146 phosphonic acids (PA) and Grignard reagents (GR). Three different functional groups, i.e.
147 methyl (M) groups, phenyl (P) groups, and propyl (Pr) groups, were grafted by both
148 techniques. Details of both grafting procedures can be found in the previous paper ([Mustafa](#)

149 [et al., 2014](#)). Modified membranes are denoted by a three letter code: MGR/PGR/PrGR
150 stand for a membrane grafted with methyl/phenyl/propyl using the Grignard grafting
151 technique; MPA/PPA/PrPA stands for a membrane grafted with methyl/phenyl/propyl using
152 the phosphonic acid grafting technique.

153 It is important to mention that even for the same functional group, both grafting techniques
154 deliver different surface chemistries ([Mustafa et al., 2014](#)). Grignard modification leads to a
155 partial replacement of the surface -OH groups of the native membranes, and to a unique
156 direct bond of the organic groups to the metal atom not involving an oxygen atom (M-R
157 bond) ([Meynen et al., 2009](#); [Rezaei Hosseinabadia et al., 2014](#)). In contrast, the reaction of
158 the phosphonic acid groups with the surface of a native membrane occurs via condensation
159 reactions with one or more OH-groups resulting in the formation of one or more oxygen
160 bridging (M-O-P-R) bonds. Figure 1 visualizes the different types of membrane surface
161 chemistry for the membranes that were used in this fouling study. As will be shown in
162 section 3.1 PPA and PrPA membranes lead to membranes with such a high hydrophobicity
163 that no water flux could be measured. As a consequence, these membranes were not
164 incorporated in this fouling investigation.

165

166 Figure 1

167

168 For most membrane types, different specimens (2 to 5) were used to study the
169 reproducibility of the results.

170

171 **2.3. Model foulants solutions**

172 As explained in the introduction, in surface and ground water DOM is a major and common
173 foulant especially in combination with inorganic salts or ions (e.g. Ca^{2+}). DOM is a mixture of
174 many different natural organic compounds that can be divided into two parts. One part
175 consists of smaller size molecules (molecular weight between a few Da to 5 kDa) known as
176 FAs. Figure 2A gives an example of the typical structure of a FAs molecule ([Buffle et al.,
177 1977](#)). The other part, known as HAs, contains large molecules (molecular weight can be
178 between 5 kDa to 50 kDa). An example of the typical structure of a HAs molecule is shown in
179 figure 2B ([Stevenson, 1994](#)).

180 FAs are fairly soluble under all conditions due to its relative high charge/polarity, while the

181 solubility of HAs depends upon different factors such as concentration of inorganic ions and
182 pH (Tipping et al., 1988). Complexation of DOM with inorganic ions increases if pH increases,
183 because of higher dissociation of the carboxylic groups of DOM (Hong and Elimelech, 1997).
184 At the same time, at high pH and high inorganic ions (especially Ca^{2+}) concentration, calcite
185 precipitates are formed.

186 In this study, a number of different aqueous HAs and FAs foulant solutions, with and without
187 inorganic ions (Ca^{2+}), were prepared to measure their fouling tendency on the different
188 membranes under examination. Concentrations of HAs, FAs, and inorganic ions (Ca^{2+}) used,
189 mimic their concentration in real surface and ground water: 10 mg/L of HAs and FAs, and 2
190 mmol/L of Ca^{2+} (Malleevialle, 1996; Volk et al., 2001). The pH of the mixtures was 6.5 -7 in all
191 cases. These conditions avoided DOM precipitation. Concentration of organic content in the
192 permeates and retentates have been determined by UV absorbance at 254 nm using a
193 UV1800 Shimadzu UV spectrophotometer CPS Tem. Controller. Total organic carbon (TOC)
194 and dissolved organic carbon (DOC) was measured using a catalytic high temperature
195 combustion instrument with selective detection of CO_2 (Multi N/C 2100, Analytic Jena, Jena,
196 Germany).

197 Figure 2

198

199 **2.4. Membrane characterization**

200 All membranes were characterized by different analytical techniques, before their use in
201 fouling tests. MWCO values were determined by cross-flow filtration of an aqueous mixture
202 of 3 polyethylene glycols of different molecular weight (200, 600 and 1500 Da) in a low
203 concentration (total concentration of 0.3 wt%). Cross-flow during filtration was 2 m/s; trans
204 membrane pressure (TMP) was adapted in order to keep the permeate flux at about 40
205 L/hm^2 . Gel permeation chromatography (GPC, a Shimadzu system equipped with a pump
206 (LC-20AT), Auto sampler (sil 20AC HT), column oven (CTO-20AC) and a refractive index
207 detector (RID 10A)) was applied to analyze the permeate and retentate samples. The applied
208 columns for GPC were an ultrahydrogel column 120 (7.8mm x 300mm) and ultrahydrogel
209 column 500 (7.8mm x 300mm) in series, used at a temperature of 40°C and with a flow of
210 0.6 ml/min. The calibration curve was made with PEG standards with Mw between 106 and
211 12200 Da.

212 Hydrophilicity/hydrophobicity of the membranes was estimated by measuring water contact
213 angles (CA) with the help of a contact angle system OCA 15 plus manufactured by Data
214 physics using the software SCA 20. In case of ceramic membranes, the measurements were
215 done on small membrane pieces that were co-modified with the applied membranes. The
216 membrane pieces were dried at 60 °C under vacuum (1×10^{-3} mbar) before measuring the CA.
217 In case of the polymeric PolyA membrane, CA was measured before and after pretreatment
218 (pretreatment: pure water filtration at flow velocity 2 m/s, TMP 5 bar for 30 min).
219 Pure water fluxes were measured before and after fouling using pure water in a cross flow
220 system using a cross-flow velocity of 2 m/s and using a TMP of 5 bar.

221

222 **2.5. Fouling measurements**

223 DOM fouling experiments were performed using model foulant (HAs and FAs) solutions with
224 and without Ca^{2+} as feed.

225 To measure the fouling tendency of all membranes under investigation, a specific procedure
226 was adopted. The procedure is detailed in [\(Mustafa et al., 2014\)](#); a brief summary is given as
227 follows.

228 Three flux measurements were performed for one complete fouling measurement for one
229 model foulant solution:

- 230 1. Pure water flux measurement before fouling (J_0), using filtration at cross flow, until a
231 stable flux was reached. Cross-flow velocity was 2 m/s, and TMP was 5 bar.
- 232 2. Flux measurement of the foulant solution by filtration in dead end (to increase the
233 fouling). TMP was 5 bar. It is important to note that in all cases, ~2 liter of model foulant
234 solution was used as feed and the filtration was performed until ~1 liter of permeate was
235 collected, and ~1 liter remained as retentate. The observed flux decline is a measure for
236 the total fouling (reversible and irreversible).
- 237 3. Finally, after fouling, again a pure water flux (J) measurement has been done by filtration
238 at cross flow, until a stable flux was reached. Cross-flow velocity was again 2 m/s, and
239 TMP again 5 bar. This filtration removes the reversible part of the fouling by forward
240 flushing, showing the chemical fouling or irreversible fouling in the remaining flux
241 decrement. Hence, in this way of working, the flux J is identified as the flux obtained
242 after physical cleaning (forward flushing of membrane surface). It is possible that after
243 forward flushing traces of reversible fouling still exist inside the pores of the membranes,

244 especially in case of fouling with FAs (relative small molecules). As HAs cannot enter into
245 the pores due to their larger molecular size compared to the pore sizes of the
246 investigated membranes, remaining HAs inside the pores is less likely but cannot be
247 completely excluded. Nevertheless, as will be clear from the results, after forward
248 flushing, the trend of the flux decline (fouling) of all investigated membranes by FAs is
249 quite similar to the trend of the flux decline (fouling) by HAs. This suggests that the
250 chances of remaining reversible fouling by FAs inside the membrane pores after forward
251 flushing, are considered to be small.

252 In this way, the ratio of the pure water flux values before and after the foulant solution
253 filtrations, " J/J_0 ", provides an indication of the amount of fouling that remains after physical
254 cleaning by forward flushing. This remaining fouling could only be removed by chemical
255 cleaning and is therefore denoted in this work as chemical fouling or irreversible fouling.
256 Chemical cleaning succeeded in recovering the original water flux J_0 in all cases, meaning
257 that no more-persistent fouling was present on the membranes.

258 All fouling results from this study will be graphically represented in the form of this
259 normalized flux J/J_0 .

260

261 **2.6. Chemical cleaning**

262 Normally, if the flux is not fully recovered after forward flushing and hence after irreversible
263 fouling, membranes are recovered by chemical cleaning using different chemicals depending
264 upon the severity of the fouling and the nature of the foulants. Usually, for organic fouling,
265 cleaning agents such as NaOH, hypochlorite etc. are applied, while for inorganic fouling or
266 scaling cleaning agents such as inorganic acids are used ([Fritzmann et al., 2007](#); [Ning, 2011](#)).

267 Specific to the current study, after each fouling measurement, all membranes were cleaned
268 by using a commercially available alkaline cleaning agent named P₃ ultrasil 110. This cleaning
269 has a double purpose: 1) it indicates if remaining foulants after forward flushing (chemical
270 fouling) could be completely removed or not and 2) it is applied as a standard regeneration
271 to make sure that no foulants of previous measurements remain. Hence, also membranes
272 that show no irreversible fouling have been cleaned.

273 The specifications of cleaning solution and filtration conditions used are as follows: 0.2- 1 %
274 wt-solution of P₃ ultrasil 110 (pH 9 - 12, conductivity 400 - 4220 $\mu\text{s}/\text{cm}$), temperature 50 - 60
275 °C, cross flow of 3-4 m/s, TMP of 0.5 - 5 bar and filtration time of 15 - 60 min (solution

276 concentration and filtration parameters changes within the given values depending upon the
 277 fouling strength) (Mustafa et al., 2014). After chemical cleaning, rinsing with pure water was
 278 done, and subsequently the pure water permeability was determined again, allowing to
 279 determine the cleaning efficiency and verify membrane stability.

280

281 **3. Results**

282 **3.1. Membrane characterization**

283 As membrane properties such as surface charge, pore size, porosity, hydrophilicity/
 284 hydrophobicity or other chemical characteristics of the membrane surface critically
 285 determine the fouling, MWCO, CA and pure water permeability have been measured for all
 286 investigated membranes, before performing the fouling tests. For almost all membrane
 287 types, different specimens (2 to 5) were used, each specimen having a slightly different
 288 quality. For the PrGR grafting, only one membrane specimen was used, as this type of
 289 grafting was only used for extra clarification of the fouling results (see section 4).

290 The pure water flux of PPA and PrPA grafted membranes was very low or even
 291 unmeasurable, due to their very high hydrophobicity, coupled to a CA close to, or higher
 292 than 90°C. The higher hydrophobicity of these membranes compared to their Grignard
 293 counterparts (PGR and PrGR) is consistent with the higher surface coverage realized by the
 294 phosphonic acid grafting method. As a consequence, these membranes were not further
 295 incorporated in this fouling investigation.

296 Table 1 gives an overview of the results of all other membranes. The ranges mentioned show
 297 the variability of the values when measured on different membrane specimens of the same
 298 membrane type.

299

300 **Table 1:** Ranges of CA, pure water permeability, and MWCO values for all investigated membrane types. Note:
 301 The CA range given for the PolyA membranes is after pretreatment. Before pretreatment CA range was 35 -
 302 45°, the decrease of the CA before pretreatment may be caused by the preservatives that are used.

Membr. ID	CA (°)	Water permeability (L/hm ² bar)	MWCO (Da)
Native	10-20	10-30	450-550
MPA	35-45	08-27	450-550
PGR	50-60	05-14	450-550
MGR	50-60	05-13	450-550

PrGR	60	10	550
PolyA	60-75	13-27	500-600

303

304 The experimental results confirm that the MWCO values do not change substantially after
 305 the different graftings, as was already revealed in our previous work (Mustafa et al., 2014).
 306 This indicates that no significant changes in pore size occurred. Notice also that the CA
 307 values of the grafted membranes increased, while their pure water fluxes decreased
 308 correspondingly, depending upon the grafting technique and the grafted functional group
 309 (~15 % for MPA grafting and ~50 - 60 % for MGR, PGR, and PrGR grafting). However, all
 310 fluxes still remain economically viable for water treatment.

311 Table 1 clearly shows that membranes with a very wide variety of surface properties are
 312 incorporated in this fouling study. 1. CA and thus polarity varies from 10° to 75°. This range is
 313 much wider than ever used in fouling studies with polymeric membranes (lowest CA used
 314 there is about 30°) (Rana and Matsuura 2010). 2. In addition the surface functionality differs
 315 largely at similar contact angle.

316

317 **3.2. Membrane fouling by DOM**

318 In this study, a number of fouling tests were performed using model solutions of the DOM
 319 fractions HAs and FAs, with and without Ca²⁺. The same tests were performed on all
 320 investigated NF membranes having a variety of surface chemistry. Moreover, for the same
 321 membrane type, different membrane specimens with different pure water fluxes (J₀) were
 322 tested in order to rule out flux effects in our conclusions.

323 Figure 3 compiles all the results of normalized flux decline, measured for all membranes.
 324 From the flux decline shown, it is obvious that all membranes show fouling behavior in
 325 between the extremes of high fouling in case of native membranes (figure 3A) and absence
 326 of fouling in case of MGR membranes (figure 3E). Two effects are shown in figure 3, and will
 327 be discussed separately: the effect of membrane hydrophobicity/hydrophilicity on HAs or
 328 FAs fouling without Ca²⁺, and the effect of Ca²⁺ addition on the fouling of the DOM fractions.
 329 Let's consider first the flux decline of all investigated membranes due to the fouling of HAs
 330 without Ca²⁺. This study reveals that very hydrophilic membranes as native ceramic
 331 membranes (CA 10 - 20°), show the strongest fouling by HAs. In comparison, the most
 332 hydrophobic membranes of this study, the PolyA membranes (CA 60 - 75°), show much

333 lower fouling compared to the native membranes. And, membranes of intermediate polarity
334 as the MGR membranes (CA 50 - 60°) show no fouling at all, while the PGR and PrGR
335 membranes having similar polarity (CA 50 – 60°) did show intermediate fouling. Obtained
336 results make it very obvious that membrane polarity alone, does not determine the strength
337 of the fouling. Thus, our results prove that the general conclusion that “more hydrophilic
338 membranes foul less”, deduced from research on polymeric membranes with a quite narrow
339 polarity and surface chemistry range, is not correct. As will be discussed in section 4, our
340 results give new insights on the fouling mechanism of DOM. These results coincide with our
341 previous reported study including HAs, meat peptone and laminarin on native, MPA, MGR
342 and PGR membranes ([Mustafa et al., 2014](#)).

343

344

Figure 3

345

346 When we look at the effect of Ca^{2+} ions on the HAs fouling, our results indicate increasing or
347 decreasing fouling depending on the surface chemistry of membranes. Native, MPA and
348 PrGR membranes show a decrease in fouling (increase in normalized flux) while PGR and
349 PolyA membranes show an increase in fouling and the MGR membranes remain unfouled.
350 The results of the polymeric membranes (PolyA) confirm the result generally known in
351 literature that “fouling is enhanced by Ca^{2+} -ions”. However, our results indicate that this
352 conclusion is not generally true, but depends on surface chemistry. We note that again no
353 correlation with membrane polarity (CA) can be found.

354 In case of FAs fouling, the trend of normalized flux decline, both in absence and in presence
355 of Ca^{2+} , is quite similar to the trend for HAs (see figure 3). Again, the native ceramic
356 membranes are the most fouled (although less than with HAs), while the MGR membranes
357 are almost not fouled or mildly fouled, and the other membranes show intermediate
358 behavior. Again, the native, PrGR and MPA membranes show less fouling in the presence of
359 Ca^{2+} , while the PolyA and PGR membranes show more fouling. In this case the MGR
360 membranes were mildly fouled without Ca^{2+} while remaining completely unfouled after the
361 addition of Ca^{2+} .

362 Comparing the results of different membrane specimens of the same membrane type, it can
363 be remarked that the extent of fouling increases as the starting pure water flux increases,
364 and this for each fouling solution. This is known in the state of the art, and is due to an

365 increase of the hydraulic resistance of the fouling layer with increasing permeation rate
366 (Hong and Elimelech 1997). Changes are however relatively small (compared to water flux
367 changes) and do not jeopardize the conclusions drawn here. To confirm this further, some
368 extra experiments with native ceramic membranes with pure water fluxes J_0 ranging from 35
369 to 133 L/hm² (factor 4) were performed, showing that fouling for the foulant solution HA 10
370 mg/L + Ca 1 mmol/L varies only from 0.4 to 0.6 (factor 1.5). Similar experiments on MGR
371 membranes with a variation of pure water fluxes J_0 ranging from 18 to 65 L/hm² confirm that
372 all these membranes remain unfouled by the mentioned foulant solution.
373 A more detailed interpretation of the obtained experimental results for all type of
374 membranes is given in section 4, when all results will have been described.

375

376 **3.3. DOM retentions**

377 From the same fouling experiments also the retentions of HAs and FAs, with and without
378 Ca²⁺, were determined for all investigated membranes. Retentions have been calculated
379 with the help of the following equation:

380

$$381 \text{ Retentions (\%)} = 100 * \text{Log (Cr/Cf)} / \text{LogVCF} \approx 100 * (1 - \text{Cp/Cr})$$

382

383 Where Cr = concentration in the retentate, Cf = concentration in the feed, Cp =
384 concentration in the permeate, and VCF = Volume Concentration Factor. In this case the VCF
385 is always about 2 (see section 2.5).

386

387 The obtained results are presented in figure 4. Figure 4 shows that the retentions of HAs
388 without Ca²⁺ through all grafted membranes are quite comparable with those of the native
389 membranes. All retentions appear to be high (> 90%), as expected for high molecular weight
390 solutes as HAs measured on NF membranes. Moreover, retentions of HAs did not change
391 significantly in the presence of Ca²⁺, and this for all membranes.

392

393 **Figure 4**

394

395 The retentions of FAs show overall much lower values compared to the HAs retentions
396 (figure 4). This corresponds to the much lower molecular mass of the FAs. Striking is the

397 significant variation of the FAs retentions over the different membranes after Ca^{2+} addition.
398 The obtained results show that, in presence of Ca^{2+} , FAs rejections decrease in case of native,
399 MGR, PrGR and MPA membranes, while increase in case of PGR and the PolyA membranes.
400 The reduction of FAs retentions is most explicit for the MPA and native membranes [figure 5
401 A&B]. Note that the influence of Ca^{2+} on the retention is proportional to its influence on the
402 fouling behavior for all membranes: less fouling coincides with lower retentions. Detailed
403 discussion of the obtained experimental results is discussed in section 4 below.

404

405 **4. Discussion of all results**

406 To explain all results mentioned in the previous sections, we consider the physicochemical
407 properties of all the investigated membranes (figure 1 and table 1) and model foulants (see
408 figure 2). This allows us to define the possibilities of hydrophilic (polar) or aromatic
409 (hydrophobic) interactions between the membranes and the foulants, and thus of fouling of
410 the investigated membranes. As an example, figure 5 visualizes all possible interactions
411 between a FAs molecule and all investigated membranes. For HAs molecules, similar
412 interactions are possible, however, due to the higher amount of aromatic rings (see figure 2)
413 the amount of possible aromatic (hydrophobic) interactions will increase. These possible
414 interactions change decisively in the presence of inorganic ions (e.g. Ca^{2+}) because of Ca-
415 DOM complexation (Hering, Morel, 1992; Dempsey, et al., 1983; Amirbahman and Olson,
416 1995).

417

418 **4.1. DOM fouling without Ca^{2+}**

419 The obtained results clearly show that the native ceramic membranes fouled more than all
420 other investigated membranes, both by HAs and FAs. This can be ascribed to the interactions
421 of the polar functional groups of DOM (COOH and OH) and the OH groups that are
422 abundantly available on the full surface of the native membranes. Various types of polar
423 interactions such as ionic interactions, electrostatic interactions, hydrogen bonding, and
424 condensation are possible (Kima et al., 2003; Ebert et al., 2004). All these polar interactions
425 lead to the strong fouling of the native membranes (figure 3A), as already indicated in our
426 previous paper (Mustafa et al., 2014).

427

Figure 5

428

429 Similar types of interactions are possible in case of the MPA grafted membranes. However,
430 the amount of possible interactions will be lower due to the reduced number of surface -OH
431 groups caused by the grafting. Moreover, the remaining -OH groups are sterically hindered
432 by the grafted -P-CH₃ groups (figure 5), together reducing interaction possibilities, leading to
433 lower fouling compared to the native membranes (figure 3B).

434 In contrast, for the PGR membranes, another type of interactions with DOM is possible e.g.
435 aromatic interactions (π - π interactions) between the grafted phenyl groups and the aromatic
436 rings of the DOM (see figure 5). As π - π interactions are always weaker than polar
437 interactions, PGR membranes are also fouled but less as compared to the native
438 membranes. This is also confirmed experimentally during the chemical cleaning of the
439 membranes after fouling, as the PGR membranes are cleanable at pH 10, while the native
440 membranes can only be cleaned at pH 12. The PolyA membranes behave very similar to the
441 PGR membranes. This is consistent with their similar surface chemistry (presence of
442 aromatic groups, see figure 5). To further confirm the similar behavior of the PGR and PolyA
443 membranes, we did an extra filtration test keeping the starting flux of both membranes
444 identical. The fouling of both membranes was exactly the same.

445 As our results show, MGR grafting significantly weakens the affinity of DOM towards the
446 membrane, resulting in extremely low fouling to no fouling at all. As mentioned previously,
447 this is ascribed to the inert character of the grafted -CH₃ groups. The fouling trend of PrGR is
448 quite similar to that of the MGR membrane. In this case the amount of fouling is a bit higher
449 than for MGR membranes, as the somewhat longer hydrocarbon chain could induce
450 somewhat higher hydrophobic (weak Van der Waals) interactions, or as the surface coverage
451 created by grafting of this longer chain could be somewhat lower (diffusion limitation effects
452 in the nanosized pores) ([Rezaei Hosseinabadia et al., 2014](#)).

453 It is important to note that in case of Grignard grafted membranes (MGR, PGR and PrGR),
454 some OH-groups remain on the surface (only partial replacement by grafting), but these
455 remaining OH groups are sterically protected by the grafted groups from direct contact to
456 the foulants, especially bulky foulants such as HAs. Smaller foulant molecules with a less
457 rigid structure such as FAs may or can have access to these sterically hindered or protected -
458 OH groups that is probably the reason why in case of pure FAs, the MGR membranes are
459 mildly fouled, and fouling has increased in case of PrGR when comparing HAs to FAs.

460 On the basis of the above mentioned experimental results and its explanations, it can be
461 concluded that the statement known in the state of the art “the higher the hydrophilicity,
462 the lower the fouling” is not always applying. Not only the polarity, but the whole of the
463 membrane surface chemistry is important and determines the potential interactions
464 between foulants and membranes. Our results give a more detailed insight, and give a clear
465 approach for anti-fouling strategies : to diminish or minimize the fouling, the surface
466 functional groups should be ideally inert for interactions with the foulants and/or the
467 interactive surface functional groups should be protected (e.g. sterically) from direct access
468 of foulants. Our work has shown that methyl grafting by the Grignard method leads to such a
469 highly “inert” surface with unparalleled low fouling.

470

471 **4.2. Effect of Ca^{2+} on DOM fouling**

472 Inorganic ions (particularly Ca^{2+}) significantly influence the DOM affinities/fouling to the
473 membranes because of Ca-DOM complexes formation ([Dempsey et al., 1983](#); [Hering and
474 Morel, 1992](#); [Amirbahman and Olson, 1995](#)). Ca^{2+} binds to DOM specifically through the
475 acidic functional groups (predominantly carboxylic groups) of DOM ([Amirbahman and Olson,
476 1995](#)). As a consequence, in the presence of Ca^{2+} , the charge and hydrophilic character of
477 DOM is reduced significantly due to the complex formation, resulting also in coiled DOM (by
478 decreased interchain electrostatic repulsion) ([Hong and Elimelech, 1997](#)). Simultaneously,
479 the aromaticity (hydrophobicity) of DOM becomes more dominant.

480 In addition, also the membrane surface chemistry can change due to Ca^{2+} addition by
481 interaction with the surface $-\text{OH}$ groups. of the native ceramic membranes, and the easily
482 accessible $-\text{OH}$ groups on the MPA membranes ([Van Gestel et al., 2002](#)). Taking into account
483 both effects of Ca^{2+} --- decreased polarity and more pronounced aromatic character of the
484 DOM foulants, and charge decrease of some of the membranes --- allows us to explain the
485 changes of the fouling caused by the addition of the inorganic ions observed in our
486 experiments. As mentioned in 4.1, for the native ceramic membranes and the MPA
487 membranes, the fouling without Ca^{2+} is mainly caused by polar interactions, and these
488 decrease substantially when Ca^{2+} is added, due to both effects. This clarifies the decreased
489 fouling for these membranes. Due to the higher amount of interacting $-\text{OH}$ groups on the
490 native membranes, the effects are more prominent for native membranes than for the MPA

491 membranes. This effect is schematically summarized in Figure 6 (left scheme), where the
492 thickness of the arrows correspond to the amount of interactions.

493 On the contrary, for the aromatic membranes, PolyA and PGR, the possible interactions (π - π
494 interactions) between membrane and foulants increase, resulting in the observed increased
495 fouling by Ca^{2+} addition. In addition, the adsorbed layer will be more extensive due to the
496 Ca-DOM complexation. This is again schematically shown in figure 6 (middle scheme).

497 In case of MGR membranes with their inert, non-interactive surface chemistry, there is no
498 real change in interactions between membrane and DOM even in presence of Ca^{2+} .
499 Therefore, MGR membranes were not fouled by DOM both in absence and presence of Ca^{2+} .
500 This is again summarized in figure 6 (right scheme). The very limited fouling observed for
501 MGR membranes in case of FAs is absent in the presence of Ca^{2+} which is consistent with the
502 reduction of hydrophilic (polar) interactions similar to native and MPA membranes
503 (interactions with the protected remaining OH-groups).

504 In case of the PrGR membrane, the decrease of fouling with Ca^{2+} addition suggests a low
505 amount of polar interactions (decreased by inorganic ions) as the reason for the mild fouling
506 of this membrane (as for native and MPA membranes). This is consistent with the expected
507 lower degree of surface coverage, and thus more remaining OH-groups, after Grignard
508 grafting of a somewhat longer alkyl chain (more diffusion effects in the nanopores during
509 grafting). As a consequence the PrGR membranes are added in the left scheme of figure 6.

510 It is important to note that, if DOM is already adsorbed on the surface of the membranes
511 before Ca^{2+} addition (irrespective of the membrane surface chemistry), then addition of Ca^{2+}
512 can increase the fouling due to layer by layer formation because of Ca^{2+} bridging, as detailed
513 in our previous article ([Mustafa et al., 2014](#)).

514 As seen from the experimental results and explained above, the presence of Ca^{2+} can either
515 increase or decrease the DOM fouling on the investigated membranes depending upon their
516 surface chemistry. This is again new and deeper knowledge, than already shown in
517 literature. The explanation confirms the conclusion of the previous section (4.1) that not
518 merely membrane polarity effects govern the fouling, but the amount and strength of
519 possible foulant-membrane interactions. These interactions are key in determining fouling in
520 ceramic as well as polymeric membranes.

521

522

Figure 6

523

524 **4.3. DOM retentions**

525 Finally, we will discuss the DOM retentions observed for all the investigated membranes
526 (figure 4). The high retentions of HAs with and without Ca^{2+} , are logical in view of the high
527 molecular mass of HAs molecules, and the corresponding strong size exclusion. The
528 retentions of FAs molecules are in the range of what one would expect for molecules of this
529 size filtrated through membranes with cut-off values of about 500 Da. Moreover, the FAs
530 retentions evolve logically with the pore size: membranes of the same type but with a higher
531 starting water flux (J_0) have lower retentions. However, the variations in FAs retentions
532 between all investigated membranes, and the changes with Ca^{2+} addition, are difficult to
533 explain. Noticeable is a similar evolution of the retentions as shown for the amount of
534 fouling in figure 6: the native, MPA and PrGR membranes show a decrease in FAs retentions
535 with Ca^{2+} , while the PGR and PolyA membranes show an increase. The FAs retentions of the
536 MGR membranes show in this case a small decrease as for the membranes with polar
537 interactions. This might indicate an influence of surface chemistry also on retentions, even
538 though the mechanism cannot yet be unravelled. It is important to note that these
539 retentions are determined in dead-end filtration conditions without stirring, inducing most
540 probably strong concentration polarization effects that can influence the retention results.
541 Experiments in cross-flow conditions would give more insight here. But this is outside the
542 scope of this study.

543

544 **5. Conclusions**

545 The fouling of the DOM fractions HAs and FAs was studied, with and without Ca^{2+} , on native
546 and grafted ceramic NF membranes and on a typical polymeric NF membrane. The observed
547 flux decline without Ca^{2+} reveals that the most hydrophilic membranes (native ceramic)
548 show the strongest fouling. Membranes of intermediate polarity (MGR) show no fouling at
549 all, while the PGR and PrGR membranes having similar polarity did show intermediate
550 fouling. The obtained results make it obvious that fouling is not determined by membrane
551 hydrophilicity as a general and sole criterion, but is influenced by the whole of the surface
552 chemistry determining the amount and strength of possible foulant-membrane interactions.
553 This signifies that the general conclusion that “more hydrophilic membranes foul less”,

554 deduced from research on polymeric membranes with a quite narrow polarity and surface
555 chemistry range, is not always true.

556 The effect of Ca^{2+} on the fouling was observed to be different for different surface
557 chemistries. Native, MPA and PrGR membranes having primarily polar-interactions with
558 DOM, show decreased fouling in presence of inorganic ions. On the contrary, PolyA and PGR
559 membranes having primarily π - π interactions with DOM, show increased fouling. Due to
560 their inert character MGR membranes remain unfouled also with Ca^{2+} .

561 The difference of HAs and FAs retentions can be logically explained by their size. However,
562 the variations as function of surface chemistry, and Ca^{2+} addition, are not obvious.

563 These new insights in the DOM fouling mechanism is valuable to steer further research for
564 understanding fouling by others type of foulants and to develop adequate antifouling
565 strategies.

566

567

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