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Nanoparticles Retention Potential of Multichannel Hollow Fiber Drinking Water Production Membrane

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1. INTRODUCTION

34
35

36 Since the 1980s, nanotechnologies occupy an increasingly important place and offer
37 opportunities in many sectors due to new properties acquired at the nanoscale [1]. The
38 applications involving engineered nanoparticles (NPs) can result in a release into the
39 environment and inevitably lead to the discharge of new and various nanometric-sized materials
40 in water of which the properties are still unclear [2–6]. It is difficult to clearly define the NPs
41 removal potential offered by a drinking water plant. Previous study [7] reports that the
42 coagulation flocculation sedimentation and sand filtration would remove 20%-90% and 60%-
43 97% respectively of NPs. The ozonation step, even if it is not initially a NPs removal step,
44 would affect the aqueous matrix and would facilitate the NPs removal. During the activated
45 carbon filtration, carbon and NPs charge and ionic strength can lead to the NPs removal [7].
46 For 30 years, membrane filtration is used alone or integrated in drinking water production line
47 and allows to obtain a clarified and disinfected water. Previous studies showed that membrane
48 filtrations can be used to distinguish by fractionation large particulate ($>18\ \mu\text{m}$), particulate (2–
49 $18\ \mu\text{m}$), colloidal/nanoparticle (10 kDa– $0.2\ \mu\text{m}$) and truly dissolved fractions ($<10\ \text{kDa}$) in river
50 water samples [8]. Membrane filtration therefore presents a great potential for NPs retention [7,
51 9–11]. It is important to clearly understand the behaviour of these NPs during the filtration, the
52 objective being to retain a maximum of NPs on the membrane surface to limit fouling of the
53 membrane in depth, in order to limit the process productivity decrease and facilitate the
54 backwash of the membranes. In fact, Decaloris et al. [12] showed that the pretreatment by ferric
55 chloride which increases the particle floc size can lead to a decrease of pore fouling and
56 enhanced backwashing efficiency but it is function of the shear stress [13]. Several researches
57 study the retention of NPs by microfiltration (MF) membrane to identify fouling mechanisms
58 occurring during the filtration. Henry and Brant [14] showed that cake filtration model describe
59 the membrane fouling by nanoparticles with hydrodynamic diameter of 91 nm. However, they
60 mentioned that under unfavourable deposition conditions (pH, ionic strength, ratio between
61 nanoparticle and pore diameters or the interfacial conditions), the NPs can pass through and
62 depositing within the MF membrane structure leading to a standard pore blocking, at least
63 during the initial stages of membrane fouling. This result is confirmed by Trzaskus et al. [15]
64 who described MF membrane fouling by five subsequent fouling stages: adsorption,
65 unrestricted transport through pores, pore blocking, cake filtration and cake maturation.
66 Trzaskus et al. [16] showed, by filtering NPs from 10 to 100 nm in monodisperse or

67 polydisperse sample, that the larger the NPs are, the faster blockage by cake filtration occurs.
68 It was proved that some settings of the filtration (molecular weight, concentration of steric
69 stabilizer and filtration pressure) significantly influence pore blockage and cake filtration [17].
70 Finally, the retention efficiency and retention mechanism may be affected by adsorption
71 phenomenon, electrostatic interactions or other interactions. In fact, smaller particles than
72 membrane pore size can be retained by membrane [9] and the presence of salts, pH and valence
73 of the cation strongly influence nanoparticles properties and interactions between themselves
74 or with the membrane and thus the occurrence and character of the fouling stages [15]. In
75 contrast, the NPs concentration of feed have no influence on fouling stages occurring but only
76 on their establishment velocity but Trzaskus et al. [15] show that the filtration resistance is
77 function of the accumulated mass.

78 For UF, it was proved that the retention of NPs is clearly transmembrane pressure (TMP)
79 dependent [18] from 60% at a TPM of 0.05 bar to less than 40% at TPM = 0.4 bar. In the same
80 way, Wu et al. [19] showed that Quantum Dots (QD) with size of 1.5 nm, 2.2 nm, 3.2 nm and
81 3.8 nm are retained at 75%, 90%, 85% and 98% respectively by a 30 kDa UF membrane at
82 TMP = 0.6 bar, against 10%, 20%, 45% and 70% respectively at TMP = 2 bar. NPs penetration
83 profiles presented by Wu et al. [19] are also dependent of NPs size vs. MWCO. The aim of this
84 study is to establish an accurate and reliable methodology allowing to clearly identify the
85 retention of NPs and the position of fouling on/in multichannel hollow fiber UF membrane.
86 Influence of NPs size, transmembrane pressure and volume concentration factor on retention
87 rate, fouling establishment or location of fouling was investigated. TMP applied during this
88 study are low pressures similar to those used in drinking water treatment plant.

89

90 **2. Materials and methods**

91 **2.1. Membranes**

92 Multichannel (7 channels) organic hollow fiber UF membranes (ALTEONTM I, SUEZ
93 aquasource[®], France), made with hydrophilic polyethersulfone (PES), were used in this study.
94 They present a 200 kDa molecular weight cut-off (MWCO) with an average nominal pore size
95 of 20 nm. The inner diameter of a channel is 0.9 mm and the external diameter of the hollow
96 fiber is 4 mm. Filtration experiments were realized for a length of 20 cm. These membranes
97 allow internal-external filtration and have an average permeability of 1050 L.h⁻¹.m⁻².bar⁻¹ with
98 a standard deviation of 50 L.h⁻¹.m⁻².bar⁻¹.

100 **2.2. Nanoparticles**

101 In agreement with the pore size, three NPs sizes are used, a smaller (1,5nm), a bigger (100nm)
102 than the membrane pore size and one close to the membrane pore size (10 nm). Silica
103 nanoparticles used (Sicastar Red-F, Micromod Partikeltechnologie GmbH, Germany) are silica
104 NPs with diameters of 10 nm (NP-10) and 100 nm (NP-100). They are labeled with rhodamine,
105 a fluorescent dye, covalently bound in the silica matrix. The absorption spectra were obtained
106 for each NPs size with a spectrophotometer (UV-VIS photoLab® 6600, WTW GmbH,
107 Germany). NPs show an absorption peak from 500 nm to 600 nm, so it is possible to excite
108 them with a green laser of 532 nm during Confocal Laser Scanning Microscopy (CLSM)
109 analysis. Nanoparticles have hydrophilic surface with Si-OH end groups. Size distributions
110 were obtained with Zetasizer Nano S (Malvern, England) and with individual monitoring
111 particle analyzer NanoSight NS300 (Malvern, England) based on Nanoparticle Tracking
112 Analysis (NTA). All measurements were performed at 20°C. Results have shown that NPs of
113 10 nm used in this study present an average size of $8.74 \text{ nm} \pm 6.6 \text{ nm}$ for a median size of 7.53
114 nm and that 100 nm NPs present an average size of $100.7 \text{ nm} \pm 40 \text{ nm}$ for a median 96.9 nm
115 for a total of about 30,000 particles analyzed for each size. Smallest NPs, hydrophilic CdTe
116 QDs (powders) coated with a proprietary mixture of low-molecular weight thiocarboxylic acid
117 (PlasmaChem GmbH, Germany) were used to prepare suspensions to be filtered. CdTe QDs
118 which can be excited with a 405 nm laser and which present a maximum emission wavelength
119 at $\lambda = 510 \pm 5 \text{ nm}$ (CdTe-510) were investigated in this study which correspond to QDs size of
120 1.53 nm (NP-1.5). The main characteristics of NPs suspensions are summarized in Table 1.

121

122 **2.3 Filtration experiments**

123 Membrane module was made by potting, in an epoxy plug at each end of the module, one
124 multichannel membrane into an external shell (PVC). For each experiment, a new
125 module/membrane was used. Then membranes were flushed with Milli-Q water (conductivity
126 of $0.8 \mu\text{S}\cdot\text{cm}^{-1}$) under 1 bar of TMP to remove residues of glycerin used for preservation of
127 membranes. All filtration experiments were performed in vertical dead-end filtration mode
128 using the lab scale setup presented in Figure 1. Pure pressurized air was connected to the tank
129 which contains NPs suspension and which was connected to the module. The feed is a
130 suspension of NPs in Milli-Q water ultrafiltered by membrane (ALTEON™ I, SUEZ
131 aquasource®, France). The feed concentrations are given in Table 1 in agreement with the limit

132 of detection. Dead-end filtration was carried out at different constant TMP which was recorded
133 with a digital manometer with record function (LEO Record, KELLER, Swiss). The permeate
134 was recorded by an electronic balance ($\Delta m = \pm 0.01$ g). All experiences were carried out at
135 room temperature ($20^{\circ}\text{C} \pm 2^{\circ}\text{C}$).

136

137 **2.4 Filtration experiments**

138 2.4.1 Flux analysis

139 Feed, permeate over the time and retentate were analyzed by fluorimeter (Jenway 6300, Bibby
140 Scientific Limited, UK) and NTA for NP-100 to determine their concentration. The permeate
141 collection beaker was wrapped with aluminum foil paper to minimize fluorescence fading of
142 NPs during the filtration runs. Optimal measurement range of NTA is from 10^7 to 10^9
143 particles. mL^{-1} so dilution was made for analysis if necessary. The aggregation, which could be
144 the cause of a greater retention, is controlled by comparing NPs size in feed and retentate. The
145 filtration was carried out until a different volume concentration factor between 200 and 800 in
146 agreement with VCF usually used in the drinking water production plants. The retentate was
147 collected and analyzed at the end of the experiments and the recovery rate was calculated [19].
148 The fouled membrane was recovered after filtration experiment and dried in a desiccator with
149 anhydrous calcium sulfate. Then, the membrane was cut after wetting in liquid nitrogen in order
150 to limit the deformation of the membrane material. The fracture was performed at different
151 lengths of the hollow fiber: $\frac{1}{4}$ - $\frac{1}{2}$ - $\frac{3}{4}$ (Figure 1) to obtain significant results and the edges of
152 membranes obtained were analyzed with CLSM and SEM.

153

154 2.4.2 Estimation of NPs number on membrane surface

155 When the NPs is retained on the membrane surface, it was decided to estimate the cake
156 thickness. Making the assumption that NPs are uniformly retained on the membrane surface
157 and assuming that the distance between two particles centers is linear and equal to a NP
158 diameter, it is possible to estimate the maximum deposition thickness over the whole membrane
159 surface, on the 7 channels by calculating the number of NPs layers deposited.

160

161 **2.5 Membrane autopsy by SEM and CLSM**

162 Confocal laser scanning microscopy (CLSM) was used in addition to scanning electron
163 microscopy (SEM) to detect presence of fluorescent NPs on membrane surface and/or in
164 membrane support. After filtration, fouled membranes were analyzed on their section by SEM

165 (JSM-6320F, JEOL) at three different magnifications (x25, x75 and x400) under 3 kV with a
166 SEI detector for magnifications of x25 and x75 and SEI detector for magnification of x400. The
167 tuning allowed the visualization of NPs on membrane surface at different zones and length of
168 the fiber and allowed to determine the deposit thickness on membrane surface with the
169 measurement tool of Image J. The thickness found was compared with CLSM results and the
170 cake thickness estimation. Membranes fouled by fluorescent NPs were also analyzed by CLSM
171 (TCS SP5, Leica Microsystems CMS GmbH, Germany). For each filtration experiment,
172 membrane was analyzed at different lengths on its section. Two scans have been made in
173 different conditions: in a visible mode to measure membrane structures and in a fluorescent
174 mode to reveal NPs signal. Membrane was analyzed in different areas of interest (Figure 1).
175 The great interest and novelty compared to previous studies are the direct analysis of the
176 membrane section against the scan according to depth [19]. The lateral resolution of CSLM is
177 better than the axial one and allows to have a high accuracy of measurement: 538.16 nm instead
178 of 5 000 nm. For the largest NPs, the excitation laser used for both scans is a green laser with a
179 wavelength of 532 nm to best excite the NPs used. During the visible scan, the RT 30/70
180 separator was used and the detection of the emission was carried out over a wavelength range
181 between 530 nm and 535 nm, making it possible to consider only the reflected light and
182 therefore to carry out a scanning representing the visible one. For fluorescence analysis, a DD
183 405/532 separator filtering the excitation wavelength, and recovery of the emission signal was
184 performed over the 575-585 nm interval. For the smallest NPs, the excitation laser used for both
185 scans is a blue argon laser with a wavelength of 488 nm to best excite the CdTe-510 used.
186 During the visible scanning, the RT 30/70 separator and the detection of the emission was
187 carried out over a wavelength range between 485 nm and 495 nm. For the fluorescence analysis,
188 a DD 488/605 separator was used, and the recovery of the emission signal was carried out over
189 the range 505-515 nm.

190

191 **2.6 Fouling models**

192 Trzaskus et al. [16] showed that rejection of NPs smaller than membrane pore size is possible
193 thanks to combination of pore blocking and/or concentration polarization phenomena during
194 filtration. They showed that during dead-end microfiltration of stable NPs suspension, fouling
195 develops in five stages (1- nanoparticles adsorption onto the membrane, 2- transport through
196 the membrane pores, 3- pore blocking, 4- cake filtration and 5- cake maturation) when
197 membrane pores are much bigger than NPs diameter. Tracking the flux decline during filtration

198 time allows to evaluate the fouling induced by NPs. During the filtration of a fluid charged with
199 particles, the resistance is modified by the accumulation of material on the membrane surface
200 or in the membrane depth. The study of the variation of normalized permeate flux (J / J_0) as a
201 function of time during filtration at constant pressure allows to identify the fouling mechanism
202 from Hermia models [20] that occur during the filtration of suspensions or during a part of the
203 filtration [19].

204

205 **3. RESULTS AND DISCUSSION**

206 **3.1 Influence of NPs size on retention**

207 3.1.1 Retention of NPs

208 Whatever the TMP applied or the VCF achieved, final retention rates calculated from
209 concentrations of retentate and permeate collected and analyzed at the end of the filtration are
210 greater than or equal to 99.9% for NP-100, greater than 99% for NP-10 and are between 77.7%
211 and 92.8% for NP-1.5. Permeates were also collected over the filtration time and concentrations
212 of each sample were determined so theoretical retention rates over the filtration time can be
213 calculated by mass balance. These theoretical retention rates, presented in Figure 2a, are
214 overestimated because NPs blocked in and/or on membrane, and therefore not recovered in the
215 retentate, are not considered. It appears that NP-100 are retained at least 99.9% from the start
216 of the experiment while retention rates of NP-10 and NP-1.5 increase with the filtration time.
217 The fouling of the membrane during firsts steps of the experiment explains this retention rate
218 increase which is directly linked to the membrane permeability decrease [16]. Figure 2b shows
219 that the filtration of smallest NP-1.5 does not induce an important permeability decrease (not
220 more than 20% in the conditions studied) even if they are retained by the membrane after few
221 minutes of filtration. The permeability decrease induced by the medium NP-10 (close to pores
222 diameter), is more important and increases with the VCF and so with the accumulation of NP-
223 10 on/in the membrane to reach about 40% in maximum operating conditions tested (TMP =
224 0.4 bar; VCF 800). As shown in Figure 2a, the retention rate of NP-10 increases with the VCF
225 which explains that the permeability decreases progressively like for NP-1.5. However, during
226 filtration of largest NP-100, retention is total since the start of the filtration and so induced a
227 strongly permeability decrease at the beginning of the filtration experiment until VCF of 100.
228 From VCF 100 to 300, the permeability decreases slowly to reach a permeability decrease value

229 superior to 90%. After a VCF of about 400, the shape of permeability curve decrease is very
230 low so the retention of NP-100 less affects the permeability.

231

232 3.1.2 Recovery of NPs

233 Recovery rate is defined as the percentage of NPs recovered in the permeate and the retentate
234 relative to the number of filtered NPs. Recovery was determined to evaluate if NPs were
235 retained based on size exclusion alone or if they were adsorbed on membrane surface and/or
236 trapped in membrane pores. High recovery is expected for NPs larger than membrane pores
237 resulting in size exclusion or for smallest NPs vs. pore size which allows nanoparticle transport
238 through the membrane without rejection. Low recovery is expected when a considerable
239 fraction of NPs were retained inside the membranes [19]. Results obtained show that NP-10
240 present a greater recovery rate than NP-1.5 and NP-100. The explanation of low recovery of
241 NP-1.5 is that NP-1.5 pass through the membrane and stay blocked in the membrane while NP-
242 100 are stopped on membrane surface and make a cake layer which stay in place at the end of
243 the filtration (Figure 3) so NP-100 are not recovered in the retentate. The recovery rate is
244 calculated thanks to final concentrations of retentate and permeate. By mass balance, it is then
245 possible to estimate the number of NPs recovered in the retentate, in the permeate and stayed
246 blocked in the membrane support and/or on membrane surface so a repartition of NPs at the
247 end of the filtration can be studied. All these values were compared to the total number of NPs
248 engaged during the filtration to obtain the Figure 4. Results show that about 20% of smallest
249 NP-1.5 filtered pass through the membrane and they are recovered in the permeate side against
250 about 10% of NP-10 and lower than 2% of largest NP-100. Repartition of NPs obtained shows
251 that only 3% of NP-1.5 smaller than membrane pore size are recovered in the retentate, the
252 retention made by blocking of NPs in/on membrane is the largest part. Trzaskus et al. obtained
253 similar results for identical pore size / NP size ratio around one log: pore clogging and
254 nanoparticle deposition later on leads to the formation of a secondary membrane, which limits
255 NP transport. Concerning NP-100, larger than membrane pore size, a low recovery is obtained
256 in the retentate and more than 85% of NPs filtered are blocked on membrane. The blocking of
257 NP-100 is mainly made by a cake on membrane surface as it is shown in Figure 3 (a,b,c), and
258 no NP-100 fluorescent signal have been visualized by CLSM in membrane support for this
259 experiment. Finally, NPs with size close to membrane pore size are the most recovered in the
260 retentate (Figure 4). Figure 5 shows a retention of NP-10 forming a tight cake layer on

261 membrane surface. During the first minutes of the filtration, NP-10 pass through the membrane
262 so retention is made on membrane too. CLSM was used to locate the NPs and so the fouling on
263 and/or in the membrane. Variation of TMP has not the same influence on the different on global
264 recovery rates for each NPs size (Figure 6). For NP-1.5, the increase of TMP increases the
265 recovery of NPs. Variation of TMP shows no significant modification of NP-10 recovery while
266 NP-100 are less recovered with the increase of TMP.

267

268 3.1.3 Location of fouling

269 3.1.3.1 Calculation method

270 The CLSM analysis of membrane samples on their section allowed to localize the NPs and
271 to obtain the deposit thickness on the membrane or the penetration profiles in the membrane.
272 The image obtained with CLSM is composed of two scans: one scan in reflective mode imaging
273 only the membrane to determine the membrane surface position and one in fluorescent mode
274 imaging the NPs fluorescent signal (Figure 5). Image analysis was performed using the software
275 Image J 1.43 (National Institutes of Health, USA). The images obtained by CLSM are formed
276 of 512 x 512 pixels. Presence detection and distribution profiles of NPs were exactly fixed at
277 the same position on the visible and fluorescent scans in order to analyze the NPs distribution
278 profile relative to the membrane surface. The maximum of the first peak in the visible scan is
279 defined like the membrane surface and the zero value is attributed to this pixel. The distribution
280 profile of nanoparticles relative to membrane surface is obtained. The deposit thickness, if there
281 is a deposit, can be estimated like the full width at half maximum. An eventual depth of NP
282 penetration in membrane can also be identified by a fluorescent intensity higher than baseline
283 (corresponding to the estimated noise level) inside the material. The penetration depth is defined
284 like the distance relative to membrane surface for which the intensity average of three
285 consecutive pixels is higher than baseline. To estimate the baseline, a clean membrane, which
286 had been rinsed with ultrapure water, was analyzed in a fluorescent scan with the same analysis
287 parameters than fouled membrane. More than fifty measurements were realized all along the
288 fiber showing homogeneity of NPs penetration.

289

290 3.1.3.2 Distribution profiles

291 As shown in Figure 7, the fluorescent signal indicates the presence of NPs throughout the
292 membrane for NP-1.5 (Figure 7a) and so confirms the passage of NPs through the membrane
293 during the filtration and the fouling of the membrane in depth. For NP-10 (Figure 7b),
294 penetration of NPs up to a thickness close to 50 μm , thickness corresponding to the skin of the
295 membrane, is observed. A tight deposit on the surface of the membrane is also identified so that
296 two fouling mechanisms can be advanced: an in-depth fouling and a cake filtration. Finally, for
297 the NP-100 (Figure 7c), a large surface deposit is visualized, explaining the strong decrease of
298 the permeability and showing a cake filtration fouling mechanism.

299

300 3.1.4 Fouling mechanisms

301 By comparing the experimental values of permeate flow rates with models proposed by Hermia
302 [20], it is possible to determine the main fouling mechanism(s) operating during filtrations. In
303 this study, high feed concentration was used so identification of each stage advanced by
304 Trzaskus et al. [16] remains difficult. The identified mechanisms do not vary with the TMP
305 applied or the VCF achieved for each size of NPs. The results show that permeability decreases
306 during the filtration of NP-100 suspension followed by a cake filtration fouling model (Figure
307 8a). This result confirms the retention rate superior to 99.9% observed from the beginning of the
308 filtration and the penetration profile obtained by CLSM. The NP-10 follows a standard blocking
309 model during the first few minutes of filtration and then a cake filtration model for the
310 remainder of the experiment (Figure 8c and 8d). NP-10 are first stopped in the membrane before
311 being deposited on the membrane surface. These both models found are confirmed by the
312 increase of retention rate during the filtration time and the penetration profile obtained which
313 reflects a NP-10 location on membrane skin and a cake layer on membrane surface. Finally, a
314 standard blocking model seems to better describe the permeability decrease during NP-1.5
315 suspension filtration (Figure 8b). In fact, penetration profile shows that NP-1.5 are stopped in
316 the membrane.

317 These experiments are realized considering the feed concentration of NPs in number, so the
318 final accumulated mass is not the same for the different NPs sizes. The figure 2c gives the
319 variation of the resistance as a function of the mass stopped by square meters. For NP-1.5, the
320 accumulated mass is small and the resistance too. The variation of resistance vs. deposit mass
321 is small. Similar results are obtained for NP-10 but the variation is doubled. Moreover, for a
322 size of NPs closes the pore size, the resistance is higher for a lower deposit mass. For NP-100,
323 the accumulated mass is important and the resistance of the cake strongly increases vs. deposit

324 mass. For the same resistance, the lower deposit mass is obtained for the NP-10 size close to
325 the membrane pore size: the accumulated mass is lower for NP-1.5 (NP penetration in the
326 membrane) and NP-10 (penetration in the skin and accumulation) meaning that the fouling
327 model involved is more constraining than for NP-100 (cake filtration). A great agreement is
328 obtained between the process parameters (Flux and retention), the CLSM penetration profiles
329 and the modelling.

330

331 **3.2 Influence of TMP**

332 Influence of the TMP variation on different parameters have been studied like on retention rate,
333 on recovery rate and on repartition of NPs relative to membrane surface. A good agreement is
334 obtained for deposit thicknesses on membrane surface measured by CLSM and SEM when
335 resolution was enough (Figure 9). The variations can be explained by the locations of
336 microscopic analysis which are not exactly the same. However, thicknesses found by mass
337 balance taking into account the recovery rate are greater than deposit measured. In fact, deposit
338 thicknesses obtained by mass balance are calculated assuming that NPs stopped are all retained
339 on membrane surface uniformly.

340

341 *3.2.1 NP-100*

342 Variation of TMP have no impact on NP-100 retention as it is shown in Figure 10a. NP-100
343 retention rate is always superior or equal to 99.9% all along the filtration experiment. However,
344 the permeability declines do not follow the same shape in function of the pressure applied and
345 it appears that the increase of TMP induces a more acute drop in permeability for a same feed
346 volume filtered, so a modification of cake structure may be expected. The permeability decline
347 is drastic during the first time of filtration (cf. part 3.1.1). Thus, if the filtration experiment is
348 conducted until a low VCF, the TMP has an influence on final permeability decrease value
349 because the slope is function of the TMP. However, if a high VCF is achieved, superior to 600,
350 the variation of final permeability value is not significant in function of TMP applied (Figure
351 10). By applying fouling models to experimental data of permeability, it is possible to obtain
352 blocking constant relative to cake filtration, k_{cf} , used in Hermia models. At constant VCF, K_{cf} ,
353 decreases with the increase of TMP. This constant is linked to the specific cake resistance which
354 can be calculated with the following equation [21]:

355

$$k_{cf} = \frac{\alpha X \mu}{A^2 TMP_0}$$

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Where α is the specific cake resistance (m.kg^{-1}), X is the NPs concentration (kg.m^{-3}), μ is the dynamic viscosity of the permeate (Pa.s), A is the membrane surface, considered as a constant over the time (m^2), and TMP_0 is the transmembrane pressure applied (Pa). This specific cake resistance was multiplied by the NPs mass stayed blocked on the membrane for each filtration experiments to evaluate the cake characteristics. For a fixed value of VCF achieved, the resistance induced by deposit of NPs increases between 0.26-0.36-0.52 m respectively for a TMP of 0.2-0.3-0.4 bar. This resistance is linked to the mass stopped and which composes the cake layer on membrane surface. Thus, investigation of deposit thickness was realized by SEM and CLSM visualization.

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At constant VCF, the influence of TMP on the percentage of NP-100 stayed blocked on the membrane have been studied. Results presented in Figure 10a are about VCF of 800, the percentages proposed here are relative to NPs number recovered in each flux relative to number of filtered NPs. When TMP increases, the NP-100 recovered in permeate and in retentate decrease so that the quantity of NPs blocked on membrane increases. The explanation is that a cake layer is formed quickly at high TMP and the cake structure was more compact (observed by SEM for a VCF=800, Figure 9): when the TMP increases less NPs are recovered in the retentate but stay blocked in the cake layer. Distribution profiles of NP-100 show a very small penetration of NP-100 in membrane. No notable variation of measured penetration depths in function of TMP applied was found. The penetration is weak due to the large size of NP (vs. pore size), from 21 μm to 30 μm , with smallest penetration for a low pressure, from 21 μm to 26 μm . These values are lower than the thickness of the membrane skin 50 μm .

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3.2.2 NP-10

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As it is shown by Figure 10b, the increase of TMP for filtration of NP-10 suspension seems to have an impact on retention and permeability. At $TMP = 0.2$ bar, the retention of NP-10 is quickly efficient so that the permeability decrease is faster and more important than at $TMP = 0.3$ or 0.4 bar. Pressure more important push NP-10 to pass through the membrane. However, the minimum retention rate observed, at the beginning at the filtration, is not lower than 97% and achievement of 99% is obtained after VCF of 40 for each case. These results explain obtaining final retention rate superior or equal to 99.9%. Differences between permeabilities

386 observed can be explained by change of recovery rate, by variations of fouling characteristics
387 (duration, constants) and by variation of fouling location in function of TMP applied.
388 Considering NP-10 repartition at the end of filtration (Figure 11), the increase of TMP decreases
389 the percentage of NPs blocked in the membrane and push NPs to pass more through the
390 membrane than at $TMP = 0.2$, involving an increase of recovered NPs in the permeate.
391 Percentage of NP-10 recovered in the retentate is important that means that NPs retained by
392 membrane are not blocked in a thick cake layer on membrane surface. In fact, SEM imaging of
393 membrane fouled by NP-10 shows a very thin deposit in comparison to NP-100 (Figure 3 and
394 Figure 12). Feed concentration of NP-10 and NP-100 are identical: even if the same number of
395 NPs is stopped by the membrane, deposit thickness will be ten times thinner and maybe less
396 stable. So, it is possible that NP-10 were recovered in the retentate by degradation of cake layer
397 during collection of retentate. Distribution profiles of NP-10 obtained by CLSM show a narrow
398 deposit on membrane surface and a penetration in depth of NPs in membrane. Penetration
399 depths found for NP-10 on all the experiments are between $46.5 \mu\text{m}$ and $63.5 \mu\text{m}$ into the
400 thickness of membrane skin ($50 \mu\text{m}$). The only definite outcome that can be advanced is that
401 for each TMP tested, NP-10 are retained by the membrane in its skin then progressively on its
402 surface. For each experiment realized, standard blocking and cake filtration have been identified
403 as fouling mechanisms describing the better macroscopic data obtained and have been
404 confirmed by CLSM observations.

405

406 3.2.3 NP-1.5

407 The increase in TMP reduces the final retention rate of NP-1.5. This result can be explained by
408 the fact that a strong TMP pushes NPs through the membrane and retention rate of 99% is
409 achieved after passage of a high permeate volume (Figure 10c). During the filtration, the fouling
410 of the membrane by NPs modifies the membrane retention efficiency. Considering the
411 variations of recovery rates in function of TMP applied, Figure 11a confirms that passage of
412 NP-1.5 through the membrane is more important when TMP is stronger. However, quantity of
413 NP-1.5 recovered in the retentate does not much vary and the percentage of NPs blocked in the
414 membrane decreases. A hypothesis which can be advanced is that at high pressure, a cake layer
415 is formed. This cake formed by NP-1.5 constitutes a secondary membrane more selective than
416 the real one and the retention is better. Clean water filtered by the cake passes through the

417 membrane and flushes the NPs deposited on membrane support resulting in a release of NPs in
418 the permeate. As shown in Figure 13, membrane seems to be flushed when TMP applied is
419 higher. This result confirms the increases of NPs quantity in permeate observed at high TMP
420 applied reported in Figure 11a.

421

422 **3.3 Influence of VCF**

423 *3.3.1 Retention rate and permeability*

424 Good reproducibility of experiments is reflected by the fact that retention rates obtained at same
425 TMP follow the same way over the filtration time for different VCF achieved with a margin of
426 error of 5% maximum. Considering NP-100, VCF have no influence on final retention rate
427 obtained as NP-100 are totally retained since the start of filtration (first sampling after 15 s
428 shows a retention rate > 99.9%). However, for NPs smaller than membrane pore size, greater
429 final retention rates are obtained for experiments conducted until high VCF. As it is shown in
430 Figure 2a, theoretical retention rate increases over the filtration time for NP-10 and NP-1.5. The
431 passage of NPs is done only during the firsts steps of the filtration, so final retention rates will
432 be higher if the filtration is conducted during a longer time. Whatever the TMP applied,
433 theoretical retention rate of 99% is achieved after a VCF of 35 and 60 for NP-10 and NP-1.5,
434 respectively (Figure 10b and 10c). Nevertheless, if the retention rate increases with filtration
435 time, the permeability decreases in the same time. So, achievement of a higher VCF will be
436 lead to a weaker final permeability.

437 *3.3.2 Recovery rate*

438 As for TMP, variation of VCF has not the same influence on global recovery rate in function
439 of NPs size (Figure 14). NP-1.5 are less recovered with the increase of VCF while NP-10 and
440 NP100 seem to be less recovered at medium VCF than at low or high VCF.

441 Considering experiments at constant filtration pressure (Figure 15), influence of VCF on
442 location of NPs can be explained. As shown previously, retention rate of NP-1.5 and NP-10
443 increase with the VCF and percentage of NPs recovered in permeate for these both NPs decrease
444 with VCF increase. Moreover, the percentage recovered in retentate for NP-1.5 decrease too so
445 it is observed that NP-1.5 are more retained in/on the membrane over the filtration run.
446 Concerning NP-10, it appears that the percentage of NPs recovered in the retentate is clearly
447 decreased and percentage blocked in/on membrane is truly increased for a variation of VCF

448 from 200 to 500. These variations observed at $TPM = 0.4$ are exactly the same at $TMP = 0.2$.
449 In fact, the increase of VCF induces that more NP-10 participate to the cake layer construction
450 so this one is more stable and less NPs are recovered in retentate. Then from VCF of 500 to
451 VCF of 800, an increase of NP-10 percentage recovered in retentate and a decrease of quantity
452 blocked in/on membrane are observed. These results may be explained by a cake degradation
453 during retentate recovery at the end of the filtration or the achievement of a limit stable deposit
454 thickness. For NP-100, results show that at low VCF, an important quantity of NPs are
455 recovered in the retentate, the same explanation than for NP-10 can be made, the cake is a little
456 thick and not stable so a large quantity of NPs is collected with retentate. At VCF 500, the cake
457 layer is very thick and structured (Figure 3) so recovery in retentate is very weakened.

458

459 *3.3.3 Membrane fouling*

460 The cake layer thickness of NP-100 observed on membrane surface increases with the VCF.
461 Figure 16 shows that a deposit thickness of $22.2 \mu\text{m}$ is found for a VCF of 200 against a deposit
462 thickness of $70.2 \mu\text{m}$ for a VCF of 500 achieved: more NPs are filtered and more the cake
463 thickness increases. This result is in agreement with permeability observed and the fact that this
464 one become almost constant after VCF of 500 (Figure 10a). Distribution profiles of NP-10 show
465 presence of NPs on membrane surface and very few in membrane skin. With the increase of
466 VCF (VCF 800), the width of first pic on fluorescent profiles increases which reflects an
467 accumulation of NP-10 on membrane surface. In the same way, distribution profiles of NP-1.5
468 show presence of NPs on membrane. At the maximum value of $VCF = 800$, a small thickness
469 cake appears on fluorescent profiles (Figure 13). However, deposit layer thicknesses of NP-1.5
470 on membranes surfaces can't be estimated due to the resolutions of CLSM and SEM.

471

472 **4. Conclusion**

473 Through this study, a methodology of accurate and reliable localization of membrane fouling
474 by fluorescent NPs used as probes was developed. The use of CLSM with a membrane analysis
475 on its section yielded penetration profiles relative to membrane surface with an accuracy of
476 538.16 nm (axial resolution of CLSM under analysis conditions used) against a pitch of 5000
477 nm with a methodology previously developed (Wu et al., 2014). The reliability of the results
478 was demonstrated by the consistency obtained by the different characterization techniques used

479 (mass balance, fouling models, microscopies). The retention potential of NPs with sizes smaller,
480 close to and bigger than UF hollow fiber pore size (20 nm) in ideal suspensions was studied. It
481 was found that 100 nm NPs were all retained (retention rate $\geq 99.9\%$) by these membranes from
482 the beginning of the filtration, the retention being carried out only on the membrane surface
483 with a very low penetration thickness (some NP-100 are detected from 20 μm to 30 μm into the
484 skin). Membrane used presents good final retention rate ($> 99\%$) for NPs of 10 nm, the retention
485 rate increasing with the VCF and with the membrane fouling establishment. Location of 10 nm
486 NPs by CLSM showed presence of 10 nm NPs on membrane surface and only in the membrane
487 skin confirming fouling models identified with macroscopic data. Finally, it has been
488 demonstrated that the NPs of 1.5 nm can be retained (retention rate $> 77.7\%$) by these UF
489 membranes, with an increase of the retention rate with the increase of VCF achieved. The
490 increase of this retention rate can be directly related to the blocking of NPs in the total
491 membrane material (surface, skin, support). The results also show that operating conditions do
492 not have influence on the fouling mechanisms established during filtration but on the
493 characteristics obtained. It has been proved that transmembrane pressure applied during
494 filtration may have an influence on cake structure, resistance of fouling or penetration of NPs
495 in membrane material. Finally, CLSM analysis in the different channels and at different lengths
496 of the hollow fiber did not reveal any preferential filtration zones by the membrane. The
497 filtration of mixed NP suspension is in progress and will be the subject of a forthcoming paper.

498

499

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506 **References**

- 507 [1] F. Gottschalk and B. Nowack, "The release of engineered nanomaterials to the
508 environment," *J. Environ. Monit.*, vol. 13, no. 5, p. 1145, 2011.
- 509 [2] P. Andujar, S. Lanone, P. Brochard, and J. Boczkowski, "Effets respiratoires des
510 nanoparticules manufacturées," *Rev. Mal. Respir.*, vol. 26, no. 6, pp. 625–637, Jun. 2009.
- 511 [3] D. Palomino, "Nanoparticules: Risques pour l'homme et l'environnement," *GWA*, vol. 89,
512 no. 12, pp. 979–990, 2009.

- 513 [4] C. Santaella, M. Auffan, A. Thiery, and J.-Y. Bottero, "Reproduire un écosystème pour
514 évaluer l'impact des nanoparticules," *Biofutur*, no. 347, pp. 46–49, 2013.
- 515 [5] A. Simon-Deckers, "Effets biologiques de nanoparticules manufacturées: influence de
516 leurs caractéristiques," AgroParisTech, 2008.
- 517 [6] R. Hischier and T. Walser, "Life cycle assessment of engineered nanomaterials: State of
518 the art and strategies to overcome existing gaps," *Sci. Total Environ.*, vol. 425, pp. 271–
519 282, May 2012.
- 520 [7] M. Troester, H.-J. Brauch, and T. Hofmann, "Vulnerability of drinking water supplies to
521 engineered nanoparticles," *Water Res.*, vol. 96, pp. 255–279, Jun. 2016.
- 522 [8] N. Wu, Y. Wyart, J. Rose, B. Angeletti, and P. Moulin, "Application of membrane
523 processes in fractionation of elements in river water," *Water Sci. Technol.*, p. wst2015444,
524 2015.
- 525 [9] D. A. Ladner, M. Steele, A. Weir, K. Hristovski, and P. Westerhoff, "Functionalized
526 nanoparticle interactions with polymeric membranes," *J. Hazard. Mater.*, vol. 211–212,
527 pp. 288–295, Apr. 2012.
- 528 [10] F. Springer, S. Laborie, and C. Guigui, "Removal of SiO₂ nanoparticles from industry
529 wastewaters and subsurface waters by ultrafiltration: Investigation of process efficiency,
530 deposit properties and fouling mechanism," *Sep. Purif. Technol.*, vol. 108, pp. 6–14, Apr.
531 2013.
- 532 [11] T. E. Abbott Chalew, G. S. Ajmani, H. Huang, and K. J. Schwab, "Evaluating
533 Nanoparticle Breakthrough during Drinking Water Treatment," *Environ. Health
534 Perspect.*, Aug. 2013.
- 535 [12] J. Decarolis, S. Hong, and J. Taylor, "Fouling behavior of a pilot scale inside-out hollow
536 fiber UF membrane during dead-end filtration of tertiary wastewater," *J. Membr. Sci.*, vol.
537 191, no. 1–2, pp. 165–178, Sep. 2001.
- 538 [13] E. Barbot, P. Dussouillez, J. Y. Bottero, and P. Moulin, "Coagulation of bentonite
539 suspension by polyelectrolytes or ferric chloride: Floc breakage and reformation," *Chem.
540 Eng. J.*, vol. 156, no. 1, pp. 83–91, 2010.
- 541 [14] C. Henry and J. A. Brant, "Mechanistic analysis of microfiltration membrane fouling by
542 buckminsterfullerene (C₆₀) nanoparticles," *J. Membr. Sci.*, vol. 415–416, pp. 546–557,
543 Oct. 2012.
- 544 [15] K. W. Trzaskus, W. M. de Vos, A. Kemperman, and K. Nijmeijer, "Towards controlled
545 fouling and rejection in dead-end microfiltration of nanoparticles – Role of electrostatic
546 interactions," *J. Membr. Sci.*, vol. 496, pp. 174–184, Dec. 2015.
- 547 [16] K. Trzaskus, M. Elshof, A. Kemperman, and K. Nijmeijer, "Understanding the role of
548 nanoparticle size and polydispersity in fouling development during dead-end
549 microfiltration," *J. Membr. Sci.*, vol. 516, pp. 152–161, Oct. 2016.
- 550 [17] K. W. Trzaskus, A. Zdeb, W. M. de Vos, A. Kemperman, and K. Nijmeijer, "Fouling
551 behavior during microfiltration of silica nanoparticles and polymeric stabilizers," *J.
552 Membr. Sci.*, vol. 505, pp. 205–215, May 2016.
- 553 [18] D. Jassby, S.-R. Chae, Z. Hendren, and M. Wiesner, "Membrane filtration of fullerene
554 nanoparticle suspensions: Effects of derivatization, pressure, electrolyte species and
555 concentration," *J. Colloid Interface Sci.*, vol. 346, no. 2, pp. 296–302, Jun. 2010.
- 556 [19] N. Wu, Y. Wyart, L. Siozade, G. Georges, and P. Moulin, "Characterization of
557 ultrafiltration membranes fouled by quantum dots by confocal laser scanning
558 microscopy," *J. Membr. Sci.*, vol. 470, pp. 40–51, Nov. 2014.
- 559 [20] J. Hermia, "Constant pressure blocking filtration laws - Application to power-law non-
560 newtonian fluids," *Trans IChemE*, vol. 60, pp. 111–120, 1982.

561 [21] A. Charfi, "Etude d'un procédé membranaire de traitement des eaux usées: effet des
562 paramètres biotiques et abiotiques sur le colmatage de la membrane," Université de
563 Carthage, 2014.
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