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Nanoparticles retention potential of multichannel hollow fiber drinking water production membrane

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Abstract

This study aims to investigate the retention potential of ultrafiltration (UF) multichannel hollow fiber membrane regarding nanoparticles (NPs). Filtration experiments of fluorescent NPs suspensions were carried out under different operating conditions to analyze the retention rate (RT), the fouling location and the membrane productivity. Fouling mechanism occurring during the experiment has been correlated with the distribution profiles of NPs obtained during the membrane autopsy by Confocal Laser Scanning Microscopy (CLSM). Results show that the large NPs are totally retained on the membrane surface. Medium NPs pass through the membrane at the beginning of the filtration and gradually, are stopped in the membrane skin before forming a deposit on the membrane surface. The retention rate of small NPs also increases over time and an in-depth fouling of the membrane (skin + support) has been identified. Mass balance and determination of NPs surface deposit thickness, in the case of a filtration cake, determined by CLSM and scanning electron microscopy (SEM) allowed the estimation of NPs amount trapped in the membrane structure (skin or support) and have been compared to the fouling resistance observed during filtration run. The CLSM analysis of the membrane on its section presents a great interest due to the high accuracy of measurement: 538.16 nm instead of 5 000 nm for previous study.

Keywords: Ultrafiltration, fluorescent nanoparticles, membrane fouling, characterization, CLSM

1. INTRODUCTION

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

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

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

2. Materials and methods

2.1. Membranes

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

2.2. Nanoparticles

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

2.3 Filtration experiments

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

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

2.4 Filtration experiments

2.4.1 Flux analysis

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

2.4.2 Estimation of NPs number on membrane surface

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

2.5 Membrane autopsy by SEM and CLSM

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

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

2.6 Fouling models

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

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

3. RESULTS AND DISCUSSION

3.1 Influence of NPs size on retention

3.1.1 Retention of NPs

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

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

3.1.2 Recovery of NPs

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

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

3.1.3 Location of fouling

3.1.3.1 Calculation method

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

3.1.3.2 Distribution profiles

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

3.1.4 Fouling mechanisms

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

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

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

3.2 Influence of TMP

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

3.2.1 NP-100

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

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

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.

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 .

3.2.2 NP-10

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

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

3.2.3 NP-1.5

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

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

3.3 Influence of VCF

3.3.1 Retention rate and permeability

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

3.3.2 Recovery rate

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

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

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

3.3.3 Membrane fouling

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

4. Conclusion

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

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

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