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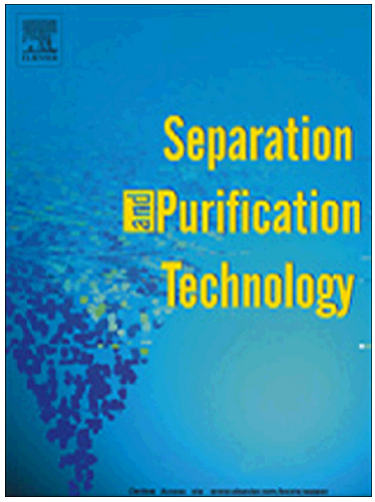

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Ultrafiltration of biologically treated domestic wastewater: How membrane properties influence performance

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Abstract

In this study, the impact of membrane properties on membrane fouling and permeate water quality was investigated. Short- and long-term laboratory scale experiments using four commercially available hollow fiber UF membranes were performed to study the impact of membrane properties on reversible and irreversible fouling. No significant differences in terms of permeate quality (i.e. biopolymer rejection) were observed over the four tested membranes. It was found that membrane characteristics including pore size, pore distribution and especially materials had a strong impact on the filtration performances in terms of both reversible and irreversible fouling. The short-term filtration tests showed that due to its specific hydrodynamic condition only the inside-out mode UF membrane was subjected to irreversible fouling. These data demonstrate the importance of membrane selection with appropriate operating conditions for optimum performances. The added value of membrane characterization to lab-scale filtration tests for membrane performance was discussed.

Keywords: Low-pressure membrane; Membrane fouling; Membrane material; Molecular weight cut-off; Wastewater reuse

1. Introduction

Due to the increasing demand for clean water, water scarcity became a global problem. Alternative sources are required to increase the available water supplies. Secondary effluent from municipal wastewater treatment plants (WWTP) is considered as an alternative source for water reclamation [1]. Over the last decade, there has been an increase in wastewater reclamation demand for the production of water suitable for irrigation, groundwater recharge or for possible indirect potable reuse [2]. As the effluent of a conventional WWTP does not meet the required water quality (e.g. presence of micro-pollutants and pathogens) additional treatment steps are required. Hence, for reuse purposes, there is a need to implement efficient treatment processes for the elimination of pathogens, micro-pollutants and organic matter [3]. Among the range of technologies available for production of water for reuse purposes, membrane technologies are of particular interest, with various full-scale plants in operation. Depending on the required water quality, different membrane types such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) can be used. A dual filtration process, in which MF or UF is used as a pre-treatment step before RO filtration, is often used to produce high quality water from secondary effluent [4].

A major limitation in membrane filtration of secondary effluent during wastewater reclamation is the significant reduction of the permeate flux caused by membrane fouling [5, 6]. Previous work were mainly focused on (i) the identification of the fractions responsible for membrane fouling [7, 8], (ii) the impact of the membrane configuration and/or nature [9, 10], (iii) the impact of the operating conditions (e.g. critical flux, cleaning procedures) [11-12] and (iv) the mechanisms involved (e.g. pore blocking, cake formation and adsorption) [11]. Studies have also investigated the impact of membrane properties on membrane fouling [12, 13]. Membranes can differ significantly in their structure and functionality, which may have an impact on membrane fouling. Indeed, Howe *et al.* (2007), showed that each membrane has

a specific chemical structure (i.e. material) that may affect its propensity for fouling [9]. Some studies investigated the impact of low-pressure membrane molecular weight cut-off (MWCO) on fouling [14-18]. However, these studies mainly used model compounds such as bovine serum albumin or humic substances [13-15] and all of them performed filtration tests with membranes manufactured for lab-scale tests instead of those used in full-scale processes. In addition, due to the cost of pilot-scale testing, there is a need for membrane users to develop affordable tools easily scalable for the selection of suitable membranes at lab-scale. Membrane characterization is a valuable tool for both users and manufacturers as it can provide information such as pure water permeability, pore size distributions, surface hydrophobicity or membrane morphology. By knowing these parameters, membrane users can more easily choose a membrane that satisfies their requirements and determine the optimal operating conditions.

This study aimed to determine the influence of membrane properties on their propensity to foul during the filtration of secondary effluent. Four commercially available polyvinylidene fluoride (PVDF) and polyethersulfone (PES) hollow fiber polymeric membranes with different MWCOs were selected. The add value of membrane characterization associated to lab-scale filtration tests in order to predict membrane performance was discussed. For this work, both hydraulic performance and permeate water quality were monitored.

2. Materials and Methods

2.1 Experimental set-up

The experiments were performed by using a bench-scale flexible filtration system according to Filloux *et al.* (2012) [8]. The filtration system was operated in dead-end mode either in outside-in or inside-out configuration, depending on the type of membrane used. Four commercially available hollow-fiber membranes that are used in full-scale systems were

tested (greater practical significance). Available membrane characteristics are presented in Table 1. UF-1, UF-2 and UF-4 membranes were operated in outside-in filtration mode and are used in full-scale wastewater treatment plant. The UF-3 membrane, which is used in full-scale drinking water applications, is used in inside-out mode.

Depending on fiber diameters, filtration modules were prepared with 4 to 8 hollow fibers to obtain a membrane surface area of 60 cm^2. A new membrane module was used for each filtration test. To avoid membrane deterioration, the mini-modules were stored in ultrapure water at 4 °C in darkness for a maximum of three weeks. The experiments were performed at ambient temperatures (19-20 °C) at a constant flux, i.e. 50 or 100 $L/m^2.h$.

Secondary effluent from an aerated activated sludge system was collected after the secondary clarifier of the Saint Julien l'Ars (SJA-SE) wastewater treatment plant (Poitiers, France). The soluble and colloidal fractions of organic matter are thought to be the main foulants of low-pressure membrane [18]. Therefore, in this study only these fractions were taken into account. Prior to the filtration tests, the raw water was filtered through 10 µm glass fibre cartridge filters (Millipore, USA) to remove suspended solids and coarse materials. Thus, the pre-filtered effluent only contained colloidal (from 10 to 0.45 µm) and soluble (<0.45 µm) fractions. The main characteristics of the secondary effluent are summarized in Table 2. Our previous study showed the impact of effluent characteristics on membrane fouling [19] and this study was performed with the same feed water (SJA-SE), chosen to represent a typical urban biologically treated municipal effluent.

2.2 Experimental procedures

The filtration performances of the four tested membranes were evaluated in terms of permeability, selectivity and organic matter rejection. Their fouling propensity was examined based on their material composition and MWCO/pore size.

Filtration tests were divided into three sets of experiments. In the first set, the pure water permeability of each membrane module was determined (*Js,w*). Because membrane is typically stored with glycerine (anti-freeze) and/or sodium bisulfide (anti-bacterial), the membrane was first washed with high purity water and 20 ppm chlorine solution (conditioning). High purity water was then filtered through the membrane at the same filtration flux used during the fouling experiment (i.e., 50 or 100 L/m².h) until a stable baseline trans-membrane pressure was obtained.

For the second set of experiments, 24 hours single cycle filtration tests were performed with pre-filtered SJA-SE to evaluate the hydraulic performances of the membranes. Membrane fouling profiles were plotted versus the total permeate throughput volume (L/m²). The repeatability of each experiment is presented in the supplementary information (SI) (see SI, Fig. A). The plots show that the deviation of the normalized specific flux decrease (*Js/Jso*) determined at 20 °C is not significantly different for duplicate experiments.

In the third set of experiments, multi-cycle filtration tests were conducted with pre-filtered SJA-SE using successive filtration cycles (i.e., multiple short periods of filtration for 15 minutes interspersed by one minute of backwash). Backwashes (BW) were performed at 50 or 100 L/m².h and carried out by reversing the direction of permeate flow (i.e., using permeate water).

At the end of each filtration experiment (single and multi-cycle filtration tests), a final backwash was performed over one minute using similar conditions to those used for membrane deconditioning. This final backwash was conducted first with high purity water and was subjected to analytical characterization (see section 2.4) in order to identify the fractions of organic matter fractions responsible for the reversible fouling. Secondly, a chemical cleaning (1 minute backwash with 200 ppm chlorine solution followed by soaking step during 30 minutes) was performed to characterize the nature of the foulants that

contributed to the irreversible fouling. Finally, to evaluate hydraulic and chemical cleaning efficiency, membrane pure water specific flux was measured. Specific flux before and after the two cleaning procedures (i.e., backwash with high purity water and chemical cleaning) was used to determine the hydraulically reversible and chemically reversible fouling (see section 2.3 for calculation, Eq. 4 & 5).

2.3 Measurements and calculations

The trans-membrane pressure (TMP) and permeate mass flow were recorded by a pressure transducer (EW-68075-32, Cole-Parmer, USA). Initial membrane permeability was calculated according to equation 1 (Eq.1).

$$Js(20°C) = \frac{J(20°C)}{TMP} \quad \text{(Eq. 1)}$$

With Js, the specific flux (i.e. membrane permeability in L/m².h.bar); J, the permeate flux (L/m².h); TMP, the trans-membrane pressure (bar).

To compare permeate flux at different temperatures (18-21 °C), the specific permeate flux was normalized at 20 °C by using equation 2 (Eq.2) and by assuming the feed water viscosity is equal to 1 Pa.s at 20°C.

$$Js(20°C) = Js(T) \times \exp(-0.0239 \times (T - 20)) \quad \text{(Eq. 2)}$$

With T, the temperature (°C).

The Unified Membrane Fouling Index (UMFI) was used to assess fouling propensity of all tested membranes. Details about the method are described elsewhere [10]. UMFI is defined by the following equation (Eq.3).

$$Jso / Js = 1 + UMFI \times Vs \quad \text{(Eq. 3)}$$

Where Jso is the initial specific flux (L/m².h.bar); Js, the specific flux (L/m².h.bar); Vs, the unit permeate throughput (L/m²).

The UMFI for single-cycle filtration tests was calculated for a Vs equivalent to Js/Jso < 0.5, while the UMFI for multiple-cycle filtration experiments was calculated for each filtration run (UMFI-i, with i representing the run number).

The backwash recovery efficiency (i.e. hydraulically reversible fouling) and the chemical cleaning recovery rate (i.e. chemical reversible fouling) were calculated according to the following equations (Eq. 4 and Eq. 5):

Backwash recovery rate (%) $$\%bw = \frac{Js,bw}{Js,w} \times 100 \quad \text{(Eq.4)}$$

Chemical cleaning recovery rate (%) $$\%c = \frac{Js,c}{Js,w} \times 100 \quad \text{(Eq.5)}$$

with Js,w, the initial specific flux measured with ultrapure water (L/m².h.bar); Js,bw, the specific flux after backwash (L/m².h.bar); Js,c, the specific flux after chemical cleaning (L/m².h.bar).

2.4 Analytical methods

2.4.1. Water characterization methods

Total Organic Carbon (TOC) was measured using a Shimadzu TOC-V-CSH. The UV absorbance at 254 nm was measured using a UV-VIS SAFAS Double Energy System 190 (UP) spectrophotometer after 0.45 µm filtration.

The apparent molecular weight distribution of TOC was estimated using High Pressure Size Exclusion Chromatography (SEC) coupled with UV/visible and fluorescence detectors in series. Size separation (Reprosil 200 SEC column, 5 µm, 300 x 8 mm, Dr Maish GmbH) was performed according to Vartiainen *et al.* (1987) [20]. The fluorescence detector was used to analyse colloidal compounds from the second order Rayleigh band (excitation and emission wavelengths set at 300 nm and 600 nm, respectively), and the UV detector was used to detect

unsaturated moieties (e.g., aromatic structures) at 254 nm. Polystyrene sulfonate standards (1400, 4300, 6800 and 13,000 Da) were used for SEC calibration.

2.4.2. Membrane characterization

Scanning electron microscopy (SEM) was used to characterize the surface and physical characteristics of the membranes (S-4500, Hitachi, Germany). Pre-conditioned membranes were dried in a desiccator and then coated with platinum in a vacuum chamber.

Contact angle measurements were conducted with a G 11 goniometer (Krüss. GmbH, Germany). The sessile drop method was used to measure the contact angles of de-ionized water (2 µL) on the surface of the membranes at room temperature. Images were captured in less than 1 s after introducing the water drop. The contact angles were calculated at least height times on different hollow-fiber membrane samples and the obtained results given as the average of the measured values with standard deviation. Contact angle could only be performed on outside/in UF membranes.

Analysis of the virus retention capability of UF during wastewater reuse is essential in order to guarantee safe water production. Membrane integrity is particularly important for reuse applications that do not require downstream RO membrane filtration, such as irrigation. A bench-scale bacteriophage retention test was carried out at constant pressure, frontal mode and ambient temperature by filtering a constant volume of viral suspension (amount of MS2 phage up to 10^6 PFU/mL prepared in 0.2 mM phosphate buffer saline solution at neutral pH). MS2 phage retention was analysed to evaluate the membrane efficiency in terms of pathogen rejection. MS2 phage was selected as microbial indicator, as it is one of the smallest non-pathogen viruses (23±1 nm). Experiments were performed in triplicate. Both feed and permeate waters were analysed by culture method (plaque forming unit, PFU) to calculate MS2 phage log removal according to Machinal *et al.,* 2009 [21] and the following equation (Eq.6):

MS2 phage log removal (log) $$LRV = \log 10 \times \left[\frac{[MS2\,feed]}{[MS2\,permeate]} \right] \quad \text{(Eq.6)}$$

with LRV, the log removal value; [MS2], the concentration (PFU/mL).

Functional groups of the membrane surface were characterized by Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) performed on dried membrane coupons (Infrared spectrophotometer Spectrum 100, PerkinElmer®, USA). Spectra were acquired between 400 and 4000 cm^{-1}. Acquisition mode was 100 scans at a resolution of 4 cm^{-1}. Liquid-liquid displacement porosimetry (LLPD) was used to determine the pore radius, r_p, i.e., the mean pore size determined from the pore permeability versus pore radius distribution. The pore permeability distribution is directly determined by the experimental flux versus pressure data using the Cantor equation (assuming cos contact angle equal to1) as described elsewhere [22, 23]. An isobutanol-methanol-water mixture was used as a wetting-displacing fluid pair, using isobutanol-methanol for wetting and water for displacement.

3. Results and discussion

3.1 Membrane characterization

The main objective of this section was to compare the different membranes based on their initial characteristics in order to predict their performance during filtration of secondary effluent. As it is not straightforward to compare and predict membrane performance solely based on pore-size estimation or pure water permeability, a full set of parameters including pore size, MS2 phage retention, morphological properties (SEM analysis), LLDP and contact angle was investigated. MS2 phage retention is strongly related to membrane characteristics; such as mean pore size and permeability (indirectly pore density) (see SI, Fig. B). Thus, the selected parameters can help membrane users to select the most suitable hollow-fiber

membranes for a given secondary effluent quality or reuse application (e.g. indirect potable reuse after RO or direct irrigation).

Results obtained for all tested membranes are summarized in Table 3. The pure water specific fluxes (at 20°C) were 875±53, 284±45, 489±93 and 312±28 L/m².h.bar, for UF-1, UF-2, UF-3 and UF-4, respectively (based on 7 determinations).

Contact angle measurements were performed to evaluate the hydrophobic/hydrophilic character of the membrane surface. The contact angle of the inside-out mode UF membrane (UF-3) could not be determined due to the small internal diameter of the fiber (I.D: 0.8 mm). According to the manufacturer data, the incorporation of polyvinylpyrrolidone (PVP) into the membrane structure makes it highly hydrophilic as compared to PES fiber [17, 24]. Contact angles for UF-1 (PES membrane), UF-2 (PVDF membrane) and UF-4 (PVDF membrane) were 66±4°, 105±2° and 87±4°, respectively, indicating that the surface of UF-1 is more hydrophilic that UF-2 and UF-4. Because PES membranes are known to be hydrophobic [25], this finding may suggest the presence of a hydrophilic additive into/onto UF-1 material. The ATR-FTIR spectrum of UF-1 shows a band at 1670 cm^{-1} that is not observed in the PES FTIR spectrum (see SI, Fig. C). As previously reported, this peak associated with C=O bond stretching, is derived from the hydrophilic agent PVP (or equivalent) that can be added to PES polymer [24].

The top surface and cross section of virgin membranes were observed by SEM (see SI, Fig. D). A rough calculation performed with Image J software and the method reported by Sun *et al.* (2007) [26], gave similar pore densities for all analysed membranes, ranging from $8x10^{13}$ to $1x10^{13}$ pores/cm^2 (see Table 3). However, SEM images of the outer (UF-1, UF-2 and UF-4) and inner (UF-3) surface of the four membranes revealed that UF-1 and UF-3 membranes exhibit slightly higher pore density leading to higher permeability than UF-2 and UF-4, characterized by a smooth surface with few dispersed pores (see SI, Fig. D).

The membranes exerted significant differences in MS2 phage retention (see Table 3). The MS2 phage log reductions were 2.0±0.3, 4.3±0.1, >5 and 2.8±0.2, for UF-1, UF-2, UF-3 and UF-4 membranes, respectively. For UF-2 and UF-3, results are in agreement with Langlet *et al*. (2009), who found MS2 phage retention ranging from 3.45±0.56 to >6 for membranes with pore sizes of 0.05 to 0.01 µm, respectively [27]. As expected, the UF membranes with the lowest pore size (i.e., UF-2 and UF-3) exerted higher MS2 phage rejection.

Next, the membranes were tested under different filtration operations (i.e. multi-cycle or long-term cycle) to determine if the experimental performance was in agreement with predictions based on membrane initial characteristics.

3.2 Filtration tests

3.2.1 Long-term single-cycle filtration experiments

3.2.1.1 Hydraulic performance

The first set of experiments consisted of 24 hour single-cycle filtration tests performed in duplicate at a constant flux of 50 L/m².h. Table 4 summarizes the hydraulic performances of the four membranes (see SI, Fig. A).

For similar filtered volumes (i.e., similar amount of DOC filtered), a more significant flux decline was obtained for UF-1 (UMFI = 0.060 m²/L) and UF-3 (UMFI = 0.027 m²/L) compared to the other two membranes (i.e. UMFI = 0.005 m²/L and 0.004 m²/L for UF-2 and UF-4, respectively). Hence, these results suggest that membranes with a higher permeability consistently exert faster fouling than membranes with lower permeability. Kim *et al.* (2008) hypothesized that this rapid fouling was attributed to a more severe pore blocking of the larger membrane pores [18].

Recovery rates after backwashing are presented in Table 4. Flux recoveries of 98±4% and 78±3% were observed for the PVDF membranes (UF-2 and UF-4, respectively), while the

PES membranes (UF-1 and UF-3) exhibited recoveries of 46±1 and 14±7%, respectively. Hence, the hydraulic irreversible fouling shows a minor contribution to total fouling for UF-2 and UF-4, but plays a predominant role for both UF-1 and UF-3. Although UF-2 and UF-4 were the less fouled membranes, previous studies also mentioned the impact of membrane materials on membrane fouling, showing similar trends. PVDF membranes were more susceptible to reversible fouling, while PES was more irreversibly fouled due to the stronger adsorption capacity of sulfone functional groups toward organic compounds (e.g., hydrogen bonding between HO group from organic compounds and O atom from SO_2 group in PES) and benzene ring-benzene ring interaction [28-31]. An increase in contact angle of UF-1, UF-2 and UF-4 was observed after 24 hours of operation (66^{o}±4 to 93^{o}±3, 105^{o}±2 to 123^{o}±1 and 87^{o}±4 to 98^{o}±3 for UF-1, UF-2 and UF-4, respectively). This result indicates that the membrane surfaces became more hydrophobic due to the accumulation of organic substances that are more hydrophobic than the membrane material. The most fouled membrane UF-1, with the highest permeability reduction, showed the greatest increase in contact angle, i.e., 41% versus 17 and 13% for PVDF membranes UF-2 and UF-4, respectively (see Table 4). With SUVA ranging from 2.8 to 3.3 L/mgC.m, SJA-SE should be considered as a humic-like enriched secondary effluent (plus data shown elsewhere [19]). The moderate SUVA value indicates a significant amount of double-bonds or aromatic structures, such as humic-like substances and aromatic amines. These organics, commonly associated to soluble microbial products formed during the activated sludge treatment [32], are mainly responsible for the hydrophobic character of the effluent and consequently their adsorption onto the membrane surface.

UF-1 is characterized by the largest pore size and the highest pore density (Table 3). Thus, results presented here suggested that UF-1 was subjected to internal fouling, which was difficult to alleviate by simple backwash. The low backwash recovery rate may result from an

extended filtration time (24 hours) compared to a short backwash time (1 min), such that the critical volume was exceeded. Similarly, despite membrane characteristics, the very low recovery rate obtained for UF-3 after hydraulic cleaning is probably the result of an inappropriate backwash procedure for inside-out flow configuration. A complete recovery was obtained for UF-2 after chemical cleaning, whereas a recovery rate of 90±2 %, 52±5 % and 80±2 % was observed for UF-1, UF-3 and UF-4, respectively. In this study, the two polymers (i.e. PVDF and hydrophilized PES) showed similar recovery after chemical cleaning, suggesting that only UF-3 was subjected to chemically irreversible fouling and the low flux recovery is more likely related to the filtration mode (outside-in filtration mode) than the nature of the material.

These results confirm the strong influence of the membrane material, filtration mode and cleaning conditions in the recovery efficiency of the membrane. The optimum conditions for cleaning depend of the filtration mode, i.e., outside-in versus inside-out.

3.2.1.2 Permeate quality and role of the colloidal fraction

The rejection of organic matter was examined during the filtration experiments. The TOC rejection rate was ≤ 5 % for UF-1 and UF-2 and 13 and 16% for UF-3 and UF-4 respectively (see SI, Table. E.1). Higher rejection was expected for UF-3 membrane because of its lower MWCO (see Tables 1 and 3). The feed water, permeate and backwash water were also characterized using an SEC-UV. The SEC-UV chromatograms are presented in SI, Fig. E.2 (results not available for UF4). UF-1 and UF-2 chromatograms were similar but different from the UF-3 profile. A significant difference was observed for the biopolymer/colloidal fraction between feed and permeate SEC profiles (i.e. first chromatographic peak, retention time (Rt) = 6 min, i.e. MW>10 kDa). The reduction of the peak intensity indicates that higher MW compounds are retained by all three membranes. It is well-established that the compounds retained by the UF membrane are mainly biopolymers (polysaccharides +

proteins) [33]. A larger difference was observed for UF-3 (see SI, Fig. E.2), which is in accordance with higher TOC removal. All membranes exert very low retention of humic and non-humic low MW substances (chromatographic fingerprint with Rt > 7 min, i.e. MW <10 kDa).

To illustrate the rejection of colloids, UF-2 permeate samples collected at different filtration times were analysed by SEC coupled with light scattering detection set to detect the 2nd Raleigh band (i.e. diffusion) (see Figure 1). The SEC chromatograms confirmed that the peak intensity of the colloid materials (Rt = 5.9 min), which are primarily composed of polysaccharides and protein-like macromolecules, decreased during filtration, reflecting increased retention. This is most likely due to the accumulation/adsorption of colloidal substances on the membrane surface and inside the membrane pores, resulting in the reduction of the average pore size.

Figure 2 presents the SEC-UV chromatograms of the UF-1, UF-2 and UF-3 backwash waters performed at the final stage with high purity water, in order to characterize the substances responsible for the hydraulically reversible fouling (not available for UF4). Backwash waters from UF-1 and UF-2 membranes consisted mainly of colloidal compounds while the sample from UF-3 indicates a wider size distribution of organic matter.

These chromatograms confirm the contribution of the high molecular weight (MW) compounds in membrane fouling (main peak intensity at Rt ~ 6min, i.e. MW >10 kDa). The less-fouled membrane with the highest flux recovery (UF-2) gave the lowest peak intensity, while the membrane with lowest flux recovery (UF-3) showed the highest peak intensity and a large retention of humic substances and lower MW compounds. These results are consistent with the organic carbon removal (i.e. TOC_{Feed}-$TOC_{Permeate}$) observed after filtration tests for the three membranes; 0.38, 0.02 and 0.74 mgC/L for UF-1, UF-2 and UF-3 respectively and a higher initial SUVA value (Calculated from SI, Table E.1 for equivalent filtered volumes).

The retention of high MW compounds is most likely due to the formation of a filter cake that reduces the apparent MWCO of the membrane [34]. However, the large amount of lower MW substances contained in the UF-3 backwash was more surprising.

According to ATR-FTIR spectra of the virgin membranes, UF-3 contains less PVP than UF-1 (i.e., larger ratio of the peak height of C=O stretch at 1670 cm^{-1} from PVP to the peak height of the aromatic bands at 1577 cm^{-1} from PES), resulting in less hydrophilic character of the membrane material (see SI, Fig. C). This can explain larger adsorption of low MW hydrophobic compounds (such as humic-like and aromatic proteins). Zheng and Croue (2012) observed that the most abundant organics in treated wastewater are hydrophobic acids isolated using XAD-8 resin (e.g., humic-like substances) [35]. Organics with stronger hydrophobic character (e.g. proteins, humic substances) adsorb onto the membrane surfaces more readily than hydrophilic

substances (polysaccharides) do [36].

The two membranes with the higher fouling potential are the PES membranes, observation that could be related again to adsorption of low MW compounds by the PVP co-polymer as suggested and similarly observed in a previous study [17]. PVP is known as hydrophilic and non-charged additive. Accordingly, the incorporation of PVP into PES material increases membrane hydrophilicity, but can also decrease membrane charge density resulting in higher humic-like substances adsorption due to less charge repulsion [37]. Furthermore, Ulbricht et al. (2008) observed the adsorption of polyphenol and polysaccharides on PES membranes during ultrafiltration of wine due to Van der Waals and electron donor-acceptor interactions [38]. Additional attractive interactions based on directed hydrogen bonds are likely to occur due to the presence of PVP additive in PES material. It has been previously reported that increasing PVP content also increases the amount of adsorbed compounds due to the affinity for polyphenol binding to PES [31]. Effluent organic matters are mixtures of polysaccharides

and aromatic containing compounds i.e., protein- and humic-like substances. These structures are enriched in carboxyl, phenol, hydroxyl and N-acetyl functional groups (e.g., amino sugars) [39], resulting in multiple possible H-bonding sites. The H-bonding adsorption mechanism described by Ulbricht et al. (2008) can be for example similarly applied to the carboxyl functional group. Indeed, the result can be explained by the existence of hydrogen bonds stronger than alcohol (i.e., OH bond can be established from carboxyl group that are richer in electrons than the oxygen atom of an alcohol and is more polarized) and the presence of hydroxyl group in effluent organic matter.

Although these substances are easily desorbed during the cleaning process, they may have a negative effect during long term filtration. This result suggests that PVP/PES membrane material might not be appropriate for the filtration of effluent enriched in polysaccharide- and humic-like substances. Furthermore, long-term fouling tests are not necessarily adapted to determine the impact of irreversible fouling. Notably, UF-1 and UF-3 require more frequent/regular backwashes due to foulant accumulation. In order to better predict membrane performance, multi-cycle filtration experiments were performed.

3.2.2 Multi-cycle filtration experiments

3.2.2.1 Hydraulic performances

Multi-cycle filtration experiments were performed to evaluate the impact of membrane properties on irreversible fouling. The secondary effluent was filtered at a flux of 50 or 100 L/m².h over 6 to 8 cycles, depending on the type of experiment conducted. Figures 3a and 3b illustrate the normalized flux as a function of the volume filtered for the four membranes, while Figures 3c, 3d and SI, Table F present the UMFI for each cycle.

The first cycle (see SI, Fig. G) revealed similar trends to those observed for the long-term filtration tests, i.e., UF-1 and UF-3 showed higher flux decline than UF-2 and UF-4.

Under both filtration conditions (i.e. 50 and 100 L/m^2.h), UF-2 showed a rapid initial flux decline before stabilisation. Thus, the UMFI-1 (UMFI for the first filtration cycle) for UF-2 was calculated after the curve break (UMFI-1 =0.0094, r^2=0.59).

The initial specific flux for the UF-2 membrane remained stable through 8 cycles for both 50 and 100 L/m².h experiments. The average UMFI values for this membrane were 0.006±0.001 and 0.007±0.001 m²/L for 50 and 100 L/m².h, respectively (same UMFI mean value), indicating that no hydraulic irreversible fouling occurred. These results confirm previous observations that the UF-2 membrane exhibits the highest flux recovery after backwash and the lowest colloidal content in backwash water.

Although UF-4 had a smaller pore density, a larger permeability and larger fiber dimensions, this membrane showed very similar results in terms of hydraulic performances than UF-2 (UMFI values and flow recovery) and thus no fouling. This observation demonstrates the difficulty in predicting membrane performance based solely on membrane properties, which highlights the importance of coupling this information with filtration trials for membrane selection.

Although UF-1 showed stronger fouling (UMFI=0.047 m²/L) except after the first backwash, a total flux recovery was achieved for the subsequent cycles (i.e. no additional irreversible fouling). The critical filtered volume (before chemical treatment is required [40]) was not reached for the UF-1, UF-2 and UF-4 membranes. Similarly, the hydraulic cleaning conditions were likely not optimized for removal of fouling that occurred during the first cycle. The frequency of the backwash is an important parameter, as demonstrated in Kim and DiGiano (2007) [41].

As previously mentioned, for the subsequent backwash cycles, UF-1, UF-2 and UF-4 showed a constant recovery of the specific flux after each backwash cycle, highlighting the effectiveness of the hydraulic cleaning.

Results obtained for UF-3 at 100 L/m².h showed that the fouling index increased from 0.071 to 0.190 m²/L for cycle 1 and 6, respectively. Under 50 L/m^2.h, the UMFI was only 0.082 L/m².h for cycle 6. Figure 3 also indicates that the initial specific flux was not restored after backwash. According to Fig.3c and 3d, the fouling index increased after each cycle when the filtered permeate volume was doubled (from 50 to 100 L/m².h), indicating that hydraulic-irreversible fouling occurred for UF-3. Thus, high fluxes promote important irreversible hydraulic fouling and require more frequent chemical cleaning.

The occurrence of irreversible fouling is well-illustrated in Figure 4. A strong flux decrease of initial flux was observed after the first backwash for the three membranes, which was likely caused by adsorption in the membrane pores at the start of filtration [42]. However, while UF-1 and UF-2 showed flux stabilisation, the initial flux of UF-3 was not restored after backwash, indicating the occurrence of irreversible fouling. Therefore, at these operating conditions (filtration and backwash fluxes and cleaning duration) the critical permeate volume was exceeded for UF-3. More foulant were accumulated per membrane surface. Thus those results suggest that beside characterization of membrane properties, operating condition such as critical permeate volume is a key parameters in membrane installation design.

3.2.2.2 Permeate quality

The water quality of the multiple-cycle filtration tests was investigated using SEC and light scattering, shown in SI, Fig. H. Figure 5 presents the difference SEC profile of the colloid peak between feed and permeate for the four permeates and their evolution from cycle 1 to cycle 8. As observed in the single-cycle filtration tests, the difference between feed water and permeate indicated the retention of biopolymer/colloidal structures by all four membranes (Figure 5). With the exception of UF-3, the three UF membranes exhibited similar permeate quality. A small increase in the peak intensity was observed between the beginning (to, cycle 1) and the end of the filtration cycle (tf, cycle 8), indicating an enhancement of the colloid

retention with time. This slight increase of the permeate quality shows the benefit of the first fouling layer as discussed previously in section 3.2.1.2 and pore narrowing.

Backwash water of UF-3 showed significantly higher chromatographic peak intensity compared to the other membranes, which is in accordance with the results shown before. The three membranes that had well-designed backwash cycles (i.e., no subject to irreversible fouling), UF-1, UF-2 and UF-4, showed a similar peak intensity.

At the end of the last filtration cycle, a chemical cleaning was performed with chlorine in order to analyze the fraction of foulant responsible for hydraulic irreversible fouling. The cleaning solutions of the PES-based membranes collected (UF-1 and UF-3) showed higher peak intensity compared to the cleaning solutions collected from the PVDF-based membranes. This observation is in accordance with the adsorption properties of PES for polysaccharide- and humic-like compounds (section 3.2.1.2).

3. 3 Discussion regarding the impact of membrane properties and their selection

From the membrane characterization results, hypothesis can be formulated for the performance of these membranes for wastewater reuse applications. It is well-known that hydrophilic membranes exhibit high fouling resistance to organic matter (i.e., lower adsorption than on hydrophobic polymer) and that highly porous membranes are subjected to internal fouling that is difficult to remove by backwash [30, 31, 43]. Thus, based on these results, UF-1 could exhibit a low irreversible fouling potential due to its low hydrophobic character (high contact angle), while its high permeability could be problematic during colloidal fouling. On the contrary, UF-2 and UF-4 showed the strongest hydrophobic character that could lead to organic matter adsorption during filtration, while they would be less influenced by internal fouling due to their low permeability. Finally, the best candidate to secondary effluent filtration appears to be UF-3, with a high hydrophilic character, high virus rejection and reasonable pure water permeability around 500 L/h m^2 bar. However, this

membrane was operated in inside-out mode and its performance could be strongly impacted by cleaning procedures.

In terms of hydraulic performances, UF-1 actually showed high initial fouling potential due to high permeability (problem of pore blocking and foulant accumulation), regulated by backwash (see Figure 5). While UF-3 also showed high permeability, high irreversible fouling potential was observed. This phenomenon was likely due to the inside-out filtration mode together with small pore size and potential adsorption properties of PES material. Although the PVDF membranes (UF-2 and UF-4) differ in MS2 phage retention, membrane pore size and fiber configuration (i.e. I.D), similar hydraulic performances were observed. Lower fouling potential was shown compared to the PES-based membranes (UF-1 and UF-3). These results suggest that the MWCO/ membrane design (I.D) does not play a major role in fouling behavior for UF-2 and UF-4 and should not be the key parameter for membranes selection. The two membranes showed similar permeate quality and backwash profile, indicating that membrane pore sizes were evened out in time.

The different fouling potential between UF2&4 and UF1&3 suggests that fouling is more related to the different membrane material rather than MWCO. Additional work should be conducted to investigate the importance of membrane material, particularly the interactions between organic matter and PES that are likely to be H-bond related (i.e., hydrogen bonding between free hydroxyl groups (as donor) and oxygen atoms projecting from the SO_2 group in PES (as acceptor)). Susanto et al. (2007) suggested a second possible mechanism associated to the replacement of water molecule at hydrophobic polymer surface by adsorbed hydrophilic solute, so called “surface dehydration” [44].

The importance of backwash and filtration mode (E/I versus I/E) was also highlighted, showing that inside-out mode is not most suitable for the filtration of secondary effluent.

In terms of permeate quality, high MW compounds removal was significant regardless the membrane characteristics. However, MS2 phage rejection strongly varied between the UF membranes. The highest rejection was found for UF-3 and the lowest for UF-1.

This methodology (membrane characterization associated to lab-scale filtration tests) could be used to determine the best compromise between high virus retention and low fouling potential. For the application of water recycling, the balance between membrane integrity (i.e., high virus removal) versus membrane hydraulic performance is important. Despite their low permeability, PVDF membranes (UF-2 and UF-4) showed low irreversible fouling and appear to be suitable membranes for direct filtration of secondary effluent, especially UF-2 due to its higher virus retention.

4. Conclusions

The influence of membrane material and MWCO on fouling and produced water quality was studied using commercially available membranes and two fouling tests performed with secondary wastewater effluent. Filtration experiments were carried out with the same secondary effluent to exclusively study the influence of membrane properties on process performance.

The results showed that lab-scale filtration tests must be performed to determine membrane fouling potential; it cannot be predicted only based on membrane characteristics.

This study indicates that membrane material is one parameter affecting the fouling of UF membranes. The lowest flux decline was observed for PVDF membranes in both short- and long-term filtration experiments, suggesting that this material is less prone to foul than other type of material. However, it is important for the reader to remember that other important parameters i.e., fiber density, module type, backwash protocol, hydraulic conditions are also known to play a major role in fouling development at industrial scale. In addition, our observation refers to only a limited number of UF membranes tested, for a single secondary wastewater effluent, at lab-scale (i.e., 60 cm^2). Additional tests on other types of waste waters could be carried out to confirm these results. Multi-cycle filtration tests indicated that only the inside-out UF membrane was subjected to irreversible fouling because its critical filtration volume was the lowest.

No significant differences were observed in terms of permeate quality. The use of size exclusion chromatography with UV detection confirmed the retention of high molecular weight compounds (biopolymers such as proteins + polysaccharides) by the four membranes, while the humic-like compounds were mostly present in permeate waters. The residual biopolymers and humic/non-humic substances may potentially result in fouling issues during reverse osmosis filtration downstream of low pressure membranes.

From these results, lab-scale filtration experiments appear as a very good support for the industry to preselect porous membranes that should be further tested at pilot scale.

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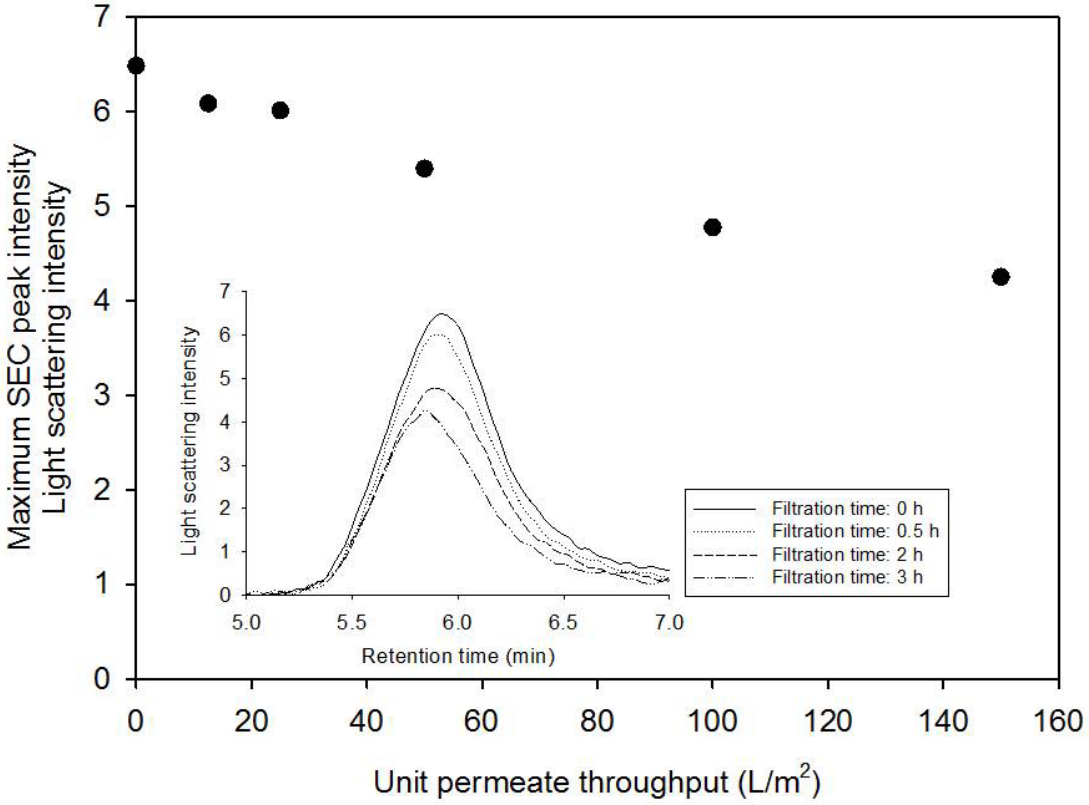


Figure 1: Evolution of the maximum chromatographic peak intensity using light scattering (Rt = 5.92 min) as a function of filtration time. Experiment performed with UF-2 membrane and a constant flux of 50 L/m².h.

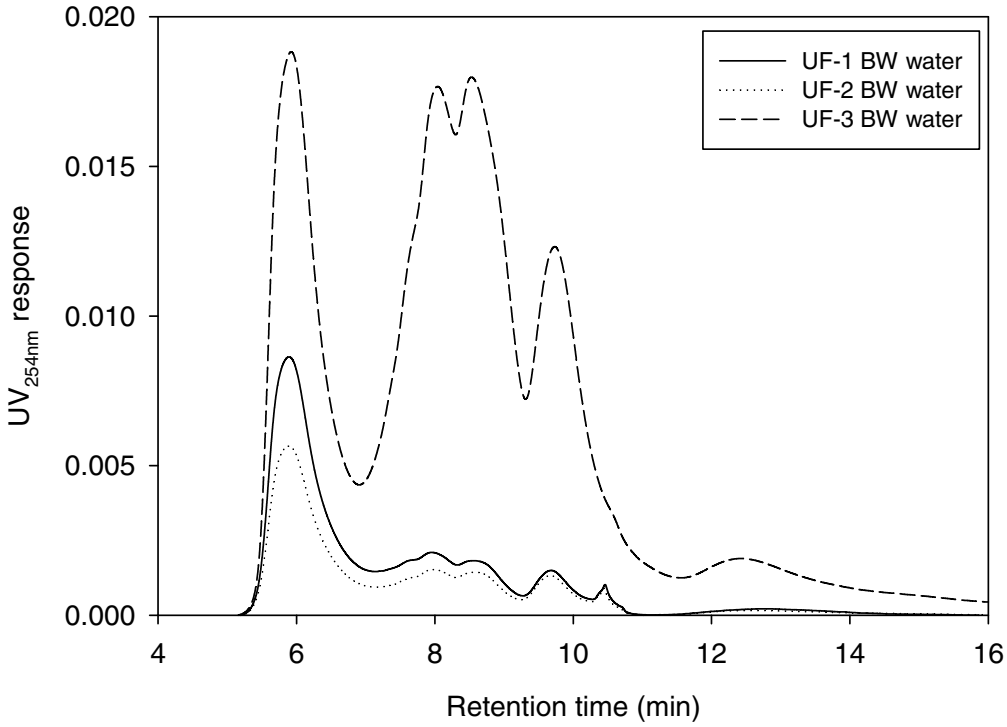
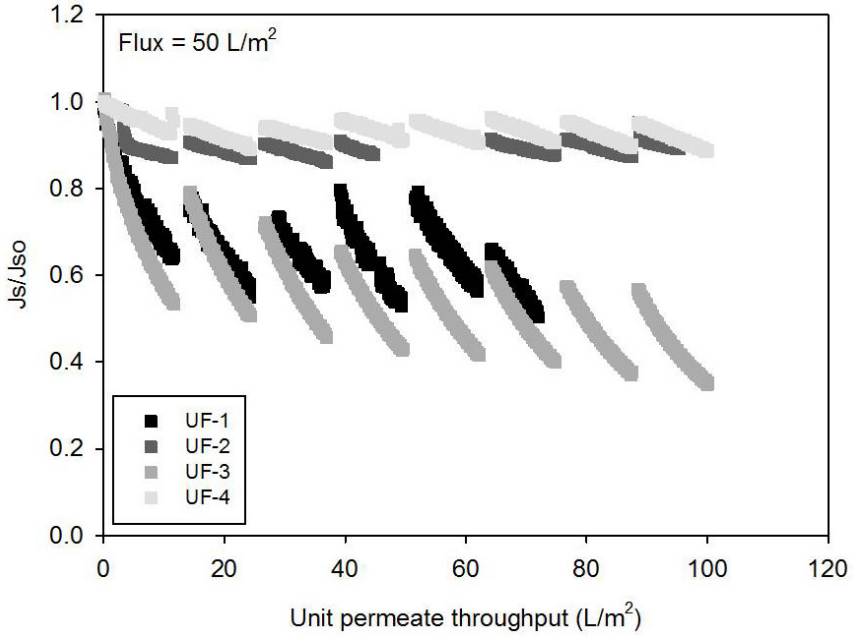
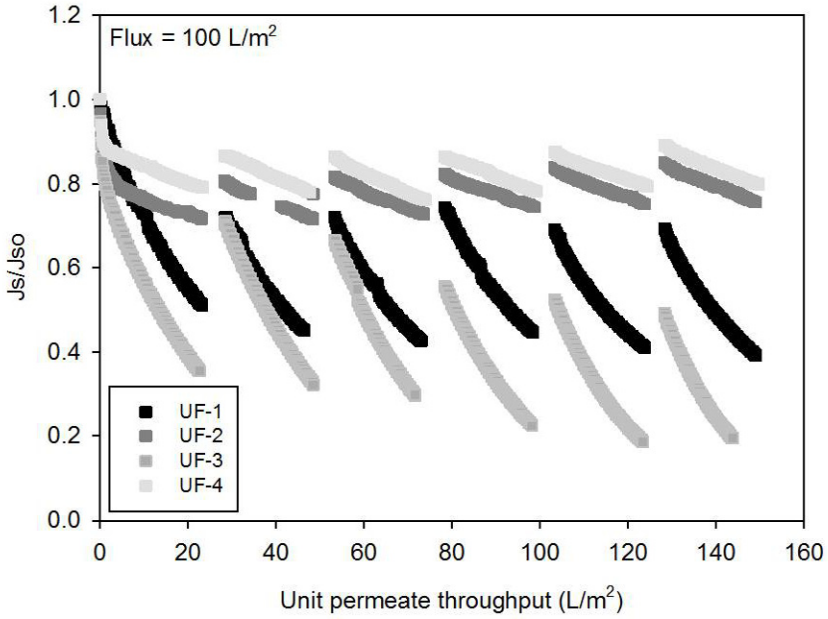


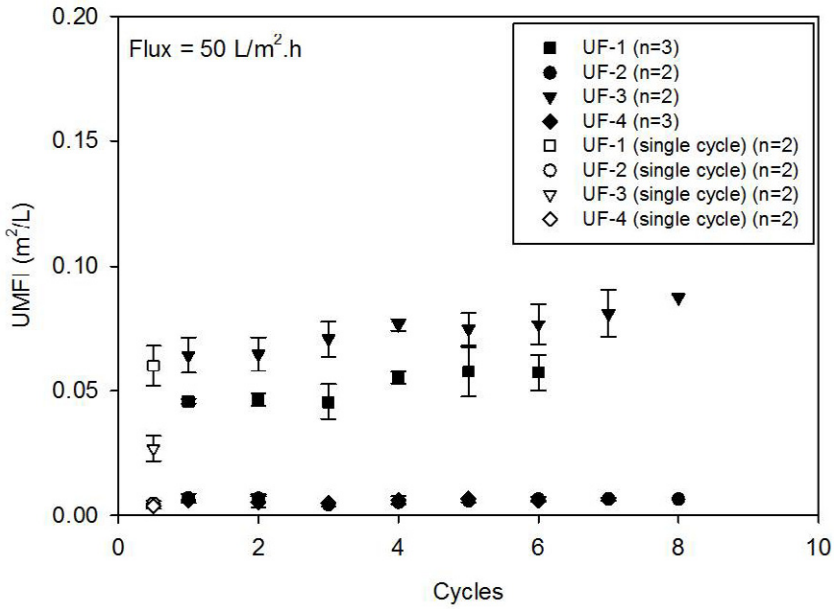
Figure 2: Normalized SEC-UV chromatograms of the backwash water (final backwash performed with MilliQ water); comparison between UF-1, UF-2 and UF-3. Normalization with $UV_{254\ nm}$ data of the backwash waters.



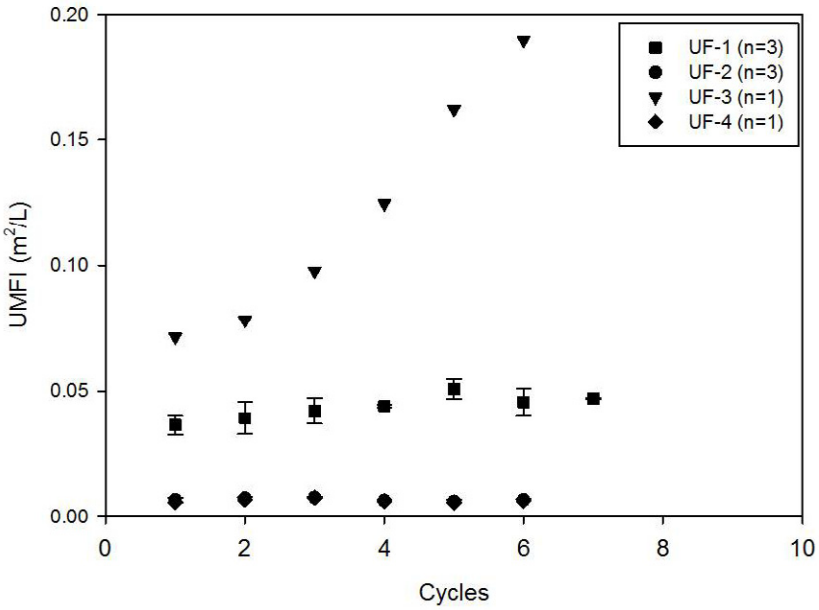
a)



b)



c)



d)

Figure 3: Normalized specific flux (with Jso, the initial specific flux of cycle 1) versus the permeate volume during multi-cycle fouling experiments with UF-1, UF-2, UF-3 and UF-4 membranes at constant flux of (a) 50 L/m².h and (b) 100 L/m².h. UMFI versus number of cycles with UF-1, UF-2, UF-3 and UF-4 membranes at constant flux of (c) 50 L/m².h and (d) 100 L/m².h.

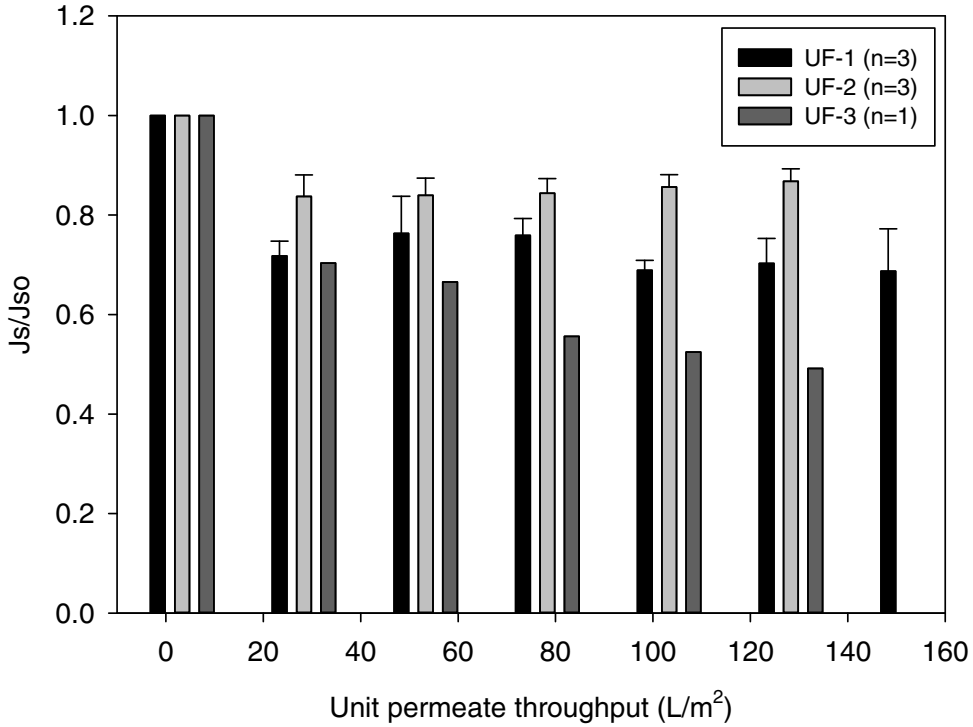


Figure 4: Initial specific flux of each filtration run versus the unit permeate throughput (L/m^2) for UF-1, UF-2 and UF-3, at a constant flux of 100 L/m².h.bar.

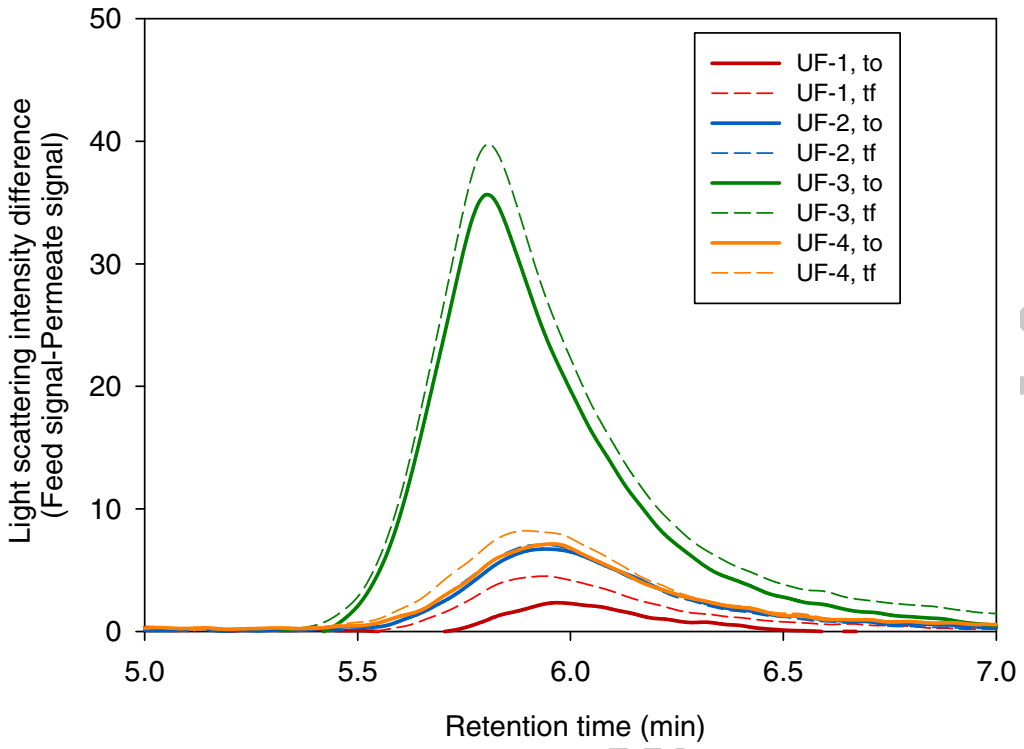


Figure 5: SEC-Fluorescence (Ex-300nm/Em-600nm) chromatograms of the Feed water-Permeate signal collected after the first (to) and the last cycles (tf) of the multi-cycle filtration experiments for UF-1, UF-2, UF-3 and UF-4.

Table 1: Characteristics of the hollow-fiber membranes (manufacturer data).

Membrane	UF-1	UF-2	UF-3	UF-4
Type	ultrafiltration	ultrafiltration	ultrafiltration	ultrafiltration
Material	PES	PVDF	PES/PVP	PVDF
Mean pore size (µm)	0.05	0.02	0.012/0.025 *	0.04
MWCO (kDa)	-	-	150**	-
Filtration mode	Outside-In	Outside-In	Inside-Out	Outside-In
Dimension, O.D/I.D (mm)	2.6/1.2	0.92/0.53	1.3/0.8	1.9/0.8

* UF-3 mean pore size (µm) = 0.012 µm calculated based on Berestovsky et al, 2001 study with r (in nm) ~ $MW^{1/2}$ (in kDa) [1] or 150kDa ~ 0.025 µm [2], ** According to membrane manufacturer.

Table 2: Main characteristics of the Saint Julien l'Ars wastewater secondary effluent (SJA-SE) (n=7).

	TOC (<10 µm) (mg/L as C)	DOC (<0.45 µm) (mg/L as C)	$UV_{254\ nm}$ (1/cm)	SUVA (l/m.mg as C)
SJA-SE	7.3 ± 0.8	6.8 ± 0.9	0.21 ± 0.01	3.0 ± 0.4

Table 3: Characteristics of the hollow-fiber membranes (experimental data).

Parameters	UF-1 PES Outside-in	UF-2 PVDF Outside-in	UF-3 PES-PVP Inside-out	UF-4 PVDF Outside-in
Pure Water specific flux, *Js,w* (L/h.m², bar, 20°C) (n=9)	897 (±14 %)	267 (±20 %)	526 (±23 %)	302 (±10 %)
Contact angle (°) (n=6)	66± 4	105± 2	highly hydrophilic*	87± 4
MS2 phage (log) (n=3)	2.0±0.3	4.3±0.1	>5	2.8±0.2
r_p** (nm) (n=4)	35±4	30±3	27±5	n.d.
Pore density *** (pores/cm²)	$8x10^{13}$	$2x10^{13}$	$4x10^{13}$	$1x10^{13}$

* Manufacturer data, ** evaluated from pore permeability versus pore size distribution (LLDP data), *** data extracted from SEM image analysis using Image J software.

Table 4: Results of the single cycle filtration tests after 24 hours of filtration using SJA-SE (n=2).

	UF-1 PES Outside-in	UF-2 PVDF Outside-in	UF-3 PES-PVP Inside-out	UF-4 PVDF Outside-in
Initial specific flux (*Jso, L/h.m^2.bar*)	963±292	208±28	658±142	270±18
Final specific flux (*Js after 24 hours, L/h.m^2.bar*)	59±2	58±1	27±5	176 (*Js after 3 hours*)
UMFI (m²/L) *	0.060±0.008	0.005±0.001	0.027±0.005	0.004±0.001
Run 1: UMFI (m²/L), r²	0.054, 0.93	0.005, 0.99	0.030, 0.99	0.004, 0.99
Run 2: UMFI (m²/L), r²	0.066, 0.99	0.004, 0.99	0.023, 0.99	0.003, 0.99
Backwash recovery rate (%)	46±1	98±4	14±7	78±3
Chemical cleaning recovery rate (%)	90 ± 2	100± 0	52 ± 5	80± 2
Contact angle (°) (n=8)	93±3	123±1	n.d.	98±3

* Calculated for Js/Jso <0.5

Highlights

- The influence of membrane properties on fouling and permeate quality was studied.
- Membrane characterization and lab-filtration tests were used to predict performance.
- Method to preselect membrane for pilot-scale trials was suggested.