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Composition and reversibility of fouling on low-pressure membranes in the filtration of coagulated water: insights into organic fractions behaviour

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ABSTRACT

The primary problem for the application of microfiltration (MF) and ultrafiltration (UF) membrane technology is membrane fouling. Such is the case that understanding membrane fouling has become one of the major factors driving MF and UF membrane technology forward. Nevertheless, identifying the constituents that most contribute to membrane fouling and quantifying how they are detached when backwashing (BW) and cleaning-in-place (CIP) are applied still remains a challenging task. The aim of the present study was to quantify membrane fouling development during filtration and membrane fouling detachment during BW and CIP in terms of membrane permeability changes and masses of inorganic and organic constituents accumulated on the membrane. The study was conducted using bench-scale MF and UF modules fed with coagulated and settled water coming from a drinking water treatment plant and operated under dead-end and cross-flow operation modes. The experiments consisted inconsecutive permeation (20 min) alternated with BW with permeate water (1.0 min) (periodically chemically assisted with NaClO and NaOH) and followed by a two-stage CIP consisting first in an oxidising and basic step (NaClO and NaOH) and second in an acidic step (citric acid). Feed, permeate, retentate (when present) and cleaning discharge streams were monitored for turbidity, total and dissolved organic carbon (TOC and DOC, respectively), UV_{254} and inorganic ions (Al, Fe, P). DOC was fractionated by high-performance size exclusion chromatography to gain insight into the behaviour of the different organic fractions. Results showed that both MF and UF membranes successfully removed turbidity, Al and Fe, whereas UV_{254} was moderately removed and TOC and DOC poorly removed, with removal percentages higher for UF than for MF. With regard to the organic fractions, the largest molecular weight compounds were moderately removed while the smallest organic fractions seemed to totally permeate through both membranes. The results also showed that foulants were poorly washed out from the

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membrane by BW, but better extracted by the two-stage CIP up to a complete detachment for some foulants.

Keywords: Backwashing; Fouling reversibility; Microfiltration; Organic fractions; Surface water treatment; Ultrafiltration

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1. Introduction

Membrane filtration processes involving microfiltration (MF) and ultrafiltration (UF) in drinking water treatment have increased in the last decades as an alternative to conventional processes such as coagulation, flocculation, sedimentation and sand filtration (SF) [1,2]. These conventional processes are often associated with limited performance, high costs, large floor space, lengthy residence times, frequent downtimes, high footprint and difficulties in coping with feed water quality fluctuations [1,3].

The primary problem for the application of MF and UF membrane technology is membrane fouling, which can reduce productivity, increases maintenance and operation costs and eventually forces membrane failure [1,4,5]. Therefore, deeper understanding of membrane fouling has become one of the major factors driving membrane technology forward.

To date, much attention has been oriented to optimise both membrane pre-treatments and membrane configuration and operation to retard membrane fouling formation [5–7]. Considerable efforts have also been directed to remove fouling from the membrane once it has been formed [8]. Membrane foulants can be removed by halting the filtration process and performing physical and/or chemical cleaning [8–10]. Periodic hydraulic backwash (BW) is the simplest and most common practice in physically controlling fouling on membranes. It consists in reversing the direction of flow so that permeate is pumped backwards through the membrane to detach foulants from it and regain (at least to a certain extent) the initial permeability. BW of MF and UF membranes is typically performed every 20–30 min and has a duration of 1–2 min. However, fouling is not always totally flushed out by BW as some substances may be strongly adhered on or within the membrane. A more effective variation of the normal BW is the so-called chemically enhanced backwash (CEB), which is a BW that incorporates chemical cleaners in the water used for the BW. The most common cleaners are oxidising (e.g. NaClO), acidic (e.g. H_2SO_4, HCl or citric acid) or basic (e.g. NaOH) agents. CEBs are usually conducted with a lower frequency compared to the BW. A third type of cleaning, still more aggressive than CEB, is the cleaning in place (CIP), which typically consists in soaking the membranes during few hours in concentrated solutions of chemical cleaners such as the ones mentioned for CEBs. Because CIPs require the shutdown of the membrane unit for several hours, it is only performed once every 2–3 months. Mass extracted by BW is commonly termed “physically reversible fouling”, while mass extracted by CIP “chemically reversible fouling”. “Irreversible fouling” refers to fouling not detached by any of the mentioned cleaning solutions [9,10].

Fouling formation can also be reduced by modifying the hydrodynamic conditions of the filtration process [6,7,11]. There are two common filtration modes. In the dead end operation mode, the entire feed water permeates frontally through the membrane, so that the retained particles left behind form a gradually thickening filtration cake on the membrane surface. Under this filtration mode, the water recovery rate is high, but the fouling tendencies are high too. In the cross-flow operation mode, feed water flows tangentially to the membrane surface and, because the system is pressurised, a fraction of water passes through the membrane. This results in two exiting streams: one which permeates through the membrane (permeate) and a second one which flows parallel to the membrane surface (concentrate or retentate). The potential advantage of the cross-flow operation mode is that the concentrate stream can carry away the foulants from the membrane surface and minimise then their accumulation on the membrane surface. On the disadvantages side, the water recovery is low in comparison with the dead-end operation mode. Whatever the operation mode, fouling is formed and periodical physical and chemical cleanings are required.

Identifying the constituents that most contribute to fouling and quantifying how they are detached when BW and CIPs are applied still remains a challenging task. Undoubtedly, understanding fouling phenomena would allow refined BW and CIP strategies, which are too often based on empirical basis and site-specific requirements [8].

Relatively abundant studies exist on the fouling formation on UF membranes, although fouling is studied in a plethora of different conditions making comparison of results sometimes difficult. Some of these studies have been carried out with synthetic solutions mainly containing model inorganic particles [12,13] or organic model compounds [14–16] often at high concentrations compared to those in real waters providing results that are not always comparable to practical situations, while some others have been carried out with real waters of different origin such as surface water [2,14,17–21], wastewater [11,22–25] and seawater [26,27], each with different fouling behaviour potentials. Besides, most of these works determine fouling formation in terms of membrane hydraulic resistance using transmembrane pressures (TMP) and fluxes based on Darcy's Law [11,15,23,24], but do not quantify the amount of foulant accumulated on the membrane.

Fewer studies exist on the reversibility of fouling when BW is applied, and even fewer when CIP is applied [8,9]. Similarly to the studies mentioned on fouling formation, many of them investigate fouling formation and detachment in terms of hydraulic resistance and recovery of flux after BW and CIP [2,12,13,16,19,24–26]. But, as pointed out by Porcelli and Judd, permeability recovery alone is itself insufficient to characterise changes in membrane fouling in response to cleaning [8]. By comparing foulant concentrations in feed, permeate and extract solution after BW and/or CIP, some researchers have attempted to estimate which constituents are preferentially removed by the membrane and which are preferentially detached by a given cleaning programme, differentiating thus between the composition of reversible and irreversible fouling [18,20–22,24,26]. Kimura et al. even reported amounts of foulants (mg) extracted from the fouled membranes [14].

Both inorganic and organic constituents have been acknowledged to contribute to membrane fouling [4,28,29]. For the purpose of gaining insight into the behaviour of the different components of natural organic matter (NOM), some of the studies mentioned have applied recently developed NOM fractionation techniques such as high-performance size exclusion chromatography (HPSEC) [11,14,18–20] or fluorescence excitation-emission matrices [18,20,30]. While most of these conclude that different organic and inorganic components do not exhibit the same fouling potential, contrasting assessments on which of them cause the reversible and irreversible fouling also exist to date. Within this framework, the objectives of this study were manifold:

(1) to quantify fouling formation on bench-scale MF and UF membranes from two perspectives: permeability decrease (hydraulics perspective) and retention of inorganic and organic constituents on the membrane (mass accumulation perspective). Given that NOM is acknowledged to play a key role in fouling, NOM was fractionated by HPSEC to obtain additional insights into the fouling potential of each organic fraction.

(2) to quantify foulant detachment when different cleaning strategies (BW(+CEB) and CIP) are applied. Foulant detachment was studied from both the point of view of permeability recovery (hydraulics perspective) and extraction of foulant amounts from the membrane (mass detachment perspective).

(3) to compare the bench-scale MF/UF with the current sequence of sand-filtration (SF) plus UF units in the full-scale drinking water treatment plant (DWTP) of Sant Joan Despí (Barcelona, Spain). This comparison aimed to provide a basis to assess the technical feasibility of replacing the current SF and UF units in the DWTP by a single membrane stage (MF or UF). The feasibility was assessed in terms of quality of the produced water, i.e. that good quality is guaranteed to ensure a good and consistent performance of subsequent reverse osmosis (RO) membrane in the DWTP in Sant Joan Despí.

(4) to compare dead-end vs. cross-flow operation modes of the bench-scale MF and UF units. This comparison was made as a first cut approach for assessing how the two modes of operation may experience differences, if any, in fouling formation, quality of permeate and fouling detachment. In this case, NOM was monitored as dissolved organic carbon (DOC) and fractionation was not performed.

2. Methods

2.1. Experimental bench-scale MF and UF devices and membrane characteristics

Bench-scale MF and UF (hereafter referred to as MF_{bs} and UF_{bs}, respectively) were operated and compared for the treatment of coagulated and settled water from the DWTP in Sant Joan Despí, Barcelona (Spain). The raw water used by the DWTP comes from the Llobregat river (and occasionally its aquifer), which presents moderately high TOC (3.4–4.9 mg/L), high turbidity (70–230 NTU) and high conductivity (1,160–1,939 µS/cm). The hardness varies in the range 245–662 mg $CaCO_3$/L, and the averaged concentrations of the main ions are 169 mg Na^+/L, 295 mg Cl^-/L, 207 mg SO_4^{2-}/L and 282 mg HCO_3^-/L. Fig. 1 shows a schematic representation of the full-scale DWTP

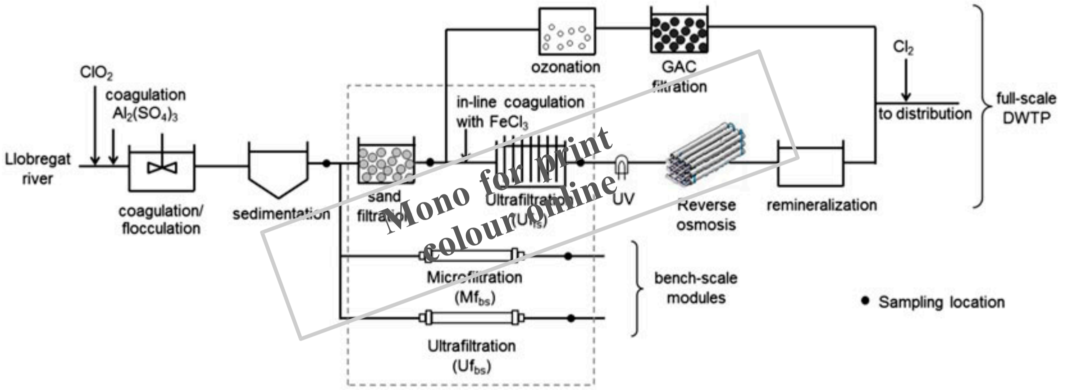

Fig. 1. Schematic representation of the DWTP of Sant Joan Despí. The treatment systems compared in this study are marked with a dashed line.

with the location where the bench-scale MF_{bs} and UF_{bs} used in this study were connected.

As shown in Fig. 1, the whole treatment train applied in the DWTP includes a conventional treatment comprised of pre-chlorination, coagulation/flocculation, subsequent sedimentation and SF. The dosage of coagulant ($Al_2(SO_4)_3$ applied (typically in the range of 60–110 mg/L) is readjusted automatically depending on the water quality and the flow to be treated. After SF, water flow is split into two halves: one undergoes ozonation and granular activated carbon filtration, while the other undergoes UF, ultraviolet (UV) irradiation, RO filtration and remineralisation. Both streams are then blended and the resulting stream subjected to post-chlorination prior to distribution. More details on the UF unit of the DWTP are given below in Section 2.3.

Both MF_{bs} and UF_{bs} membranes, made of polysulfone (PS), were assessed employing bench-scale outside-in hollow fibre modules operated under constant pressure mode (1.2 bar) and especially designed to work either under dead-end or cross-flow (tangential) filtration modes. The modules were provided by Polymem and their main characteristics are shown in Table 1. As it can be seen, MF_{bs} and UF_{bs} were identical apart from the difference in pore size.

Feed water was pumped to the membrane modules by means of a centrifugal pump (IML S.A.U., model MS100M). Appropriate combinations of valve positions allowed to select the direction of the trans-membrane flux during filtration cycles and BW episodes in either dead-end or cross-flow operation modes. The ratio between concentrate and permeate flow rates under cross-flow filtration mode was 50%. During filtration, no recirculation of permeate (or retentate) was made. During BW, flux was reversed using a peristaltic pump (Heidolph, model Pump drive PD5001) and permeate was forced through the membrane in an in-out mode. A layout of the experimental set-up is shown in Fig. 2.

Table 1
Characteristics of the MF_{bs} and UF_{bs} membrane modules provided by the manufacturer (Polymem)

	MF_{bs}	UF_{bs}	UF_{fs}
Filtration mode	Out-in		Out-in
Membrane material	PS		PVDF
Fibre external diameter (mm)	1.4		1.0
Surface area (m)/module	0.01		55.7
Nominal MWCO (kDa)	–	300	–
Nominal Pore size (μm)	0.1	0.08	0.02
Maximum TMP (bar)	1.5		1.0
Maximum TMP during BW (bar)	2.0		–
Maximum temperature (°C)	35		40
pH range	2–12		5–10

2.2. Experimental procedure for bench-scale filtration experiments

Before each experiment, a filtration test with deionised water was conducted in dead-end mode at

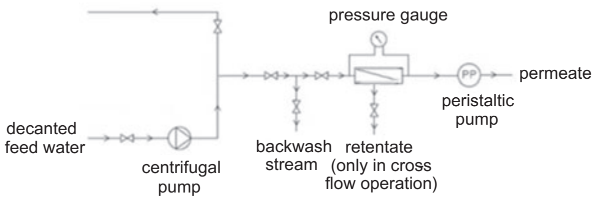

Fig. 2. Layout of the experimental setup for both MF_{bs} and UF_{bs} devices (allowed to be operated under dead-end or cross-flow mode each).

a TMP of 1.2 bar without recirculation of permeate for 15 min and then with recirculation until constant permeate production. TMP (Pa) and flow rate (Q) ($m^3\ s^{-1}$) were monitored. TMP was measured by a pressure gauge (Keller Group, model Leo 3) and permeate flux by timed collection of permeate in a volumetric flask. Both parameters allowed to calculate the permeability of the membrane (P) ($L\ m^{-2}\ bar^{-1}\ s^{-1}$) according to the equation:

$$P = \frac{Q}{\mathrm{TMP} \cdot S} \cdot k \qquad (1)$$

where S is the membrane area (m^2) and k is the temperature normalisation factor (corrected to 20°C). This P value was used as a baseline measurement of the cleaned membrane.

Experiments were then conducted with decanted water over a period of 200 min of consecutive permeation (20 min at a constant TMP of 1.2 bar) and BW (1.0 min at a TMP of 1.8 bar). Additional CEBs based on a combination of NaClO (7 mg/L) and NaOH (pH 10–11) were made every 3 BWs. The BW and CEB conditions were adopted after a previous study [31]. The total volume of feed water filtered was 4.0 L, of which approx. 0.29 L were used for BW.

The permeability of the membrane during the filtration experiments was periodically monitored according to Eq. (1), together with water quality for feed and permeate (and retentate in cross-flow experiments). The BW residuals were also collected into a separate tank as a composite sample for chemical analysis to determine which foulants were preferentially removed by BW. Each experiment was generally conducted in duplicate to ensure consistency of results.

At the end of each filtration experiment, a two-stage CIP was applied to recover the membrane permeability loss due to fouling during the experiment. The membranes were soaked first for 90 min with a NaOH solution (pH 10–11) in combination with NaClO (200 mg/L) (hereafter termed CIP-B) and subsequently for 30 min with a citric acid solution (pH 3–4) (hereafter termed CIP-A). These reagents were selected in accordance with the routine maintenance cleans performed at the DWTP of Sant Joan Despí. Analysis of discharges after CIP-B and CIP-A was carried out to identify components most removed by these cleaning strategies.

2.3. Comparison against the UF unit in the full-scale plant

Unlike the MF_{bs} and UF_{bs} modules, the full-scale UF stage in the DWTP (hereafter referred to as UF_{fs}) does not receive directly decanted water. Instead, decanted water passes first through SF, and it is this sand-filtered water that, after in-line coagulation with $FeCl_3$ (at a dose of 220 μg/L), is passed through UF_{fs} (Fig. 1). The combined SF and UF_{fs} treatments are referred to as SF + UF_{fs} hereafter.

The UF_{fs} stage consists of 0.02 μm-pore size submerged polyvinylidene difluoride (PVDF) hollow fibre UF membranes (ZeeWeed 1000, GE Water & Process Technologies–ZENON, USA) operating under an outside-in mode at constant flux (0.012 L/(s m^2)). The main characteristics of the UF_{fs} membranes are also shown in Table 1. The UF_{fs} stage consists of a total of nine chambers each accommodating nine cassettes with 57 modules each, totalling 4104 modules (with a total membrane surface area of 229,000 m^2). The UF_{fs} modules are periodically backwashed to remove hydraulic reversible fouling from the membrane. The permeation and backwash cycle durations are 45 and 10 min, respectively. Additionally, after approx. 60,000 m^3 of permeate production (which broadly corresponds to every 5–6 d) a more intense CIP with NaOH + NaClO and acid is performed.

The in-line coagulation with $FeCl_3$ aims at favouring the removal of NOM and, in particular, residual Al remaining after the $Al_2(SO_4)_3$-based coagulation step on the UF membrane. The removal of Al is crucial because it has been found to be detrimental to down-flow RO membranes even at low concentrations.

2.4. Analytical methods

Water was analysed in terms of turbidity, TOC, UV_{254}, Al, Fe and P. Turbidity is an indicator of particulate fouling potential. TOC and UV_{254} are indicative of the organic load and character that can foul the membrane. Al, Fe and P were suspected to be the main inorganic foulants in our system and were selected for this study. Samples were collected at sterile vials and stored at 4°C until analysis in the laboratory. Turbidity was analysed by nephelometry (Hach 2100 AN IS Turbidimeter), TOC by oxidative combustion and infrared-detection (Shimadzu V CPH) and UV_{254} by spectrophotometry (Hach DR 5000). Al, Fe and P were analysed by inductively coupled plasma-atomic emission spectrometer (Perkin Elmer Optima 4300 DV).

Fractionation of DOC was conducted by HPSEC using a Toyopearl TSK HW-50S weak cation exchange gel filtration column (250 × 20 mm) coupled to online UV_{254}, organic carbon (OC) and organic nitrogen (ON) detectors by DOC-Labor (Karlsruhe, Germany).

The fundamentals of the technique are reported in detail by Huber et al. [32]. Briefly, it is based on size exclusion liquid chromatography whereby organic compounds in a 0.45 μm-filtered aqueous sample are fractionated into five subfractions according to their molecular weight (MW) operationally defined as: (1) biopolymers (BP, with MW >20,000 g/mol, including polysaccharides, polypeptides, proteins and amino sugars), (2) humic substances (HS, with MW of approx. 1,000 g/mol, including fulvic and humic acids), (3) building blocks (BB, with MW between 300 and 500 g/mol, including hydrolysates of humic substances), (4) low MW acids (LMWA, with MW <350 g/mol, mainly including monoprotic organic acids) and (5) low MW neutrals (LMWN, with MW <350 g/mol, including alcohols, aldehydes, ketones, sugars and amino acids). The OC retained in the chromatographic column is termed the non-chromatographic fraction. The detection limit of this method for each fraction was 10 μg (C)/L.

3. Results

3.1. Feed water characteristics

The average composition of the decanted water during the course of the study is reported in Table 2.

Turbidity, TOC and UV_{254} in feed water averaged 1.76 NTU, 4.1 mg/L and 0.080 abs/100 cm, respectively. Al, Fe and P, the most abundant inorganic species, were found at averaged concentrations of 364, 23 and 43 μg/L, respectively. As mentioned above, the former is of particular concern in many DWTP as it represents a potential threat to RO membranes.

DOC concentration averaged 3.5 mg/L. The 15% difference with respect to TOC indicated that, after the coagulation/decantation stage, a fraction of the organic load was still in the form of particulate or colloidal OC. With regard to the DOC composition, the chromatographic fraction accounted for 97% of total DOC. A major percentage of it (45%) arises from HS, while BB and LMWN represent 24–26%, respectively. BP accounted for the remaining 5%, while LMWA was detected at <1%. Comparison with published data reveals that this DOC composition is within the typical range for untreated surface water and groundwater [12,30]. Since the majority of NOM has a size below the nominal MWCO of the studied membranes (see Table 1), poor rejection of NOM by these MF and UF membranes was anticipated. Measured specific UVA_{254} (SUVA) was 2.40 L/(mg m) and denoted moderate aromaticity of NOM [33].

3.2. Performance of MF_{bs} and UF_{bs} membranes under dead-end operation mode

3.2.1. Permeability evolution

Fig. 3 shows the evolution of the normalised permeability (i.e. the permeability divided by the initial permeability P_0) during a filtration experiment for both MF_{bs} and UF_{bs} membranes operated under

Table 2
Average feed water quality. Confidence intervals at a confidence level of 95% for all cases where replicates were performed. Number of analysed samples: 75 (for pH, turbidity and UV_{254}), 14 (for TOC, Al, Fe and P), 4 (for DOC fractions)

		Units	Feed water
pH		pH units	7.6 ± 0.2
Turbidity		NTU	1.76 ± 0.19
TOC		mg/L	4.1 ± 0.2
UV_{254}		abs/100 cm	0.080 ± 0.006
Al		μg/L	364 ± 51
Fe		μg/L	23 ± 9
P		μg/L	43 ± 14
DOC		μg/L	3467 ± 466
Non-chromatographic		μg/L	120 ± 164
Chromatographic	BP	μg/L	180 ± 85
	HS	μg/L	1516 ± 121
	BB	μg/L	768 ± 224
	LMWN	μg/L	854 ± 342
	LMWA	μg/L	<10
SUVA		L/(mg m)	2.40

dead-end filtration mode. Duplicates run for every experiment differed less than 5%, and only one of the two replicates for each experiment is plotted.

In both cases, P/P_0 profile showed an initial severe decline that levelled off at 0.4 for UF_{bs} and 0.5 for MF_{bs} by the end of the experiment. The application of periodic BW(+CEB) resulted in slight and momentary increases in P/P_0 for both membranes (recovering ca. 15–19% of the lost permeability). This indicated that BW(+CEB) removed part of the fouling (i.e. reversible fouling) but also that this P/P_0 increase never attained 1.0 meaning that a substantial fraction remained on/in the membrane (i.e. irreversible fouling). The reversible fouling may be hypothesised to be mainly due to cake formation (amenable to be washed out), while the persistent irreversible fouling on the long term may be due, at least partially, to blocking of the membrane pores [4]. Differences between BW and BW(+CEB) were not appreciable, suggesting that fouling was removed by shear effects rather than by chemical reactions with NaClO and NaOH under CEB conditions. Only when a CIP was applied at the end of experiment, permeability was restored to the pre-experiment value.

The general trend of P/P_0 shown in Fig. 3 is in agreement with Peiris et al. [20], who carried out UF of surface water under similar conditions (permeation duration of 30 min and BW duration of ca 2 min) and reported recoveries of the initial permeability of <10% when BWs were applied and of 65–75% when chemical cleaning based on NaClO and citric acid in sequence was employed. In contrast, when treating surface water by UF (permeation duration of 30 min and BW duration of 10 min), Wray et al. [21] found that most of the total fouling observed (>70%) was hydraulically reversible. The longer BW duration compared to the present study might explain their larger recovery of the initial permeability.

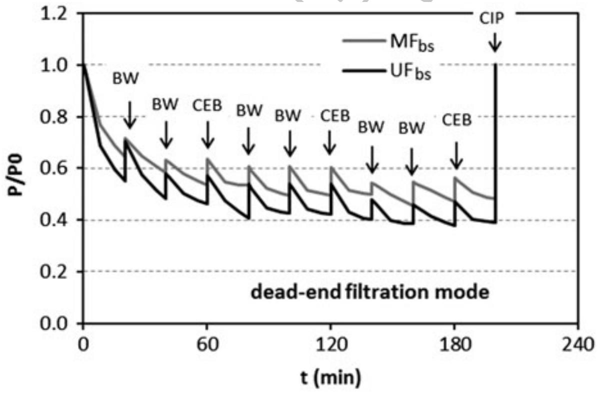

Fig. 3. Evolution of normalised permeability (P/P_0) for MF_{bs} and UF_{bs} membranes operated under dead-end filtration mode.

Comparing both membranes, UF_{bs} suffered from a higher permeability loss than MF_{bs} (Fig. 3). This was probably due to the higher amount of foulants retained by the UF_{bs} membrane (as described in the coming sections), which could add an additional resistance to the flow. It might also be due to a major blocking of membrane pores in UF_{bs} caused by particles and colloids with similar size as UF_{bs} pores that would however pass through MF_{bs} pores [4,13]. This was consistent with the lower removal percentages observed by MF_{bs} (Fig. 4). As pore blocking depends on the relative size between particles and colloids and the membrane pores, the inverse behaviour (i.e. more pore blocking in MF than UF) can also be observed if particles and colloids mainly have a similar size as MF pores [15,16,19].

3.2.2. Removal of feed water constituents

With regard to bulk parameters and inorganic ions, MF_{bs} and UF_{bs} membranes yielded a similar water quality (Fig. 4(a)). Turbidity was removed by >95%, UV_{254} by 20–25%, Al by 71–73% and Fe by 78%, while P totally passed through the UF_{bs} membrane (not plotted in Fig. 4(a)).

Concerning organic constituents, lower removals and more differences were observed between MF_{bs} and UF_{bs} (Fig. 4(b)). UF_{bs} clearly performed better than MF_{bs} at removing organic matter. The percentages removed by UF_{bs} for TOC, DOC, BP and HS were 10, 4, 43 and 7%, respectively, while they were 4%, <1, 19 and 5%, respectively, by MF_{bs}. This difference can be attributed to size-exclusion effects, whereby the narrower pores in UF_{bs} (0.08 μm, see Table 1) better retained fractions than those in MF_{bs} (0.1 μm). This is particularly appreciable for the larger fraction BP (with MW >20,000 g/mol), whose removal was up to 43% for UF_{bs} but 19% for MF_{bs}. However, for smaller HS (MW ≈1,000 mg/L), the removal was approximately the same (7–5%) for both membranes. The smallest fractions (BB, LMWN and LMWA) seemed to totally permeate through both MF_{bs} and UF_{bs} membranes (not plotted in Fig. 4(b)).

These removal percentages of bulk parameters and inorganic ions were consistent with those reported in published studies performed under comparable conditions (pH of 6.5–8, Al concentrations in the range of 100–590 μg/L, membranes with 0.1 μm pore size or cut-off of 100 kDa): 68–95% (for turbidity) [13,17], 34% (for UV254) [13], 75% (for Al) [14], >97% (for Fe) [17].

Also the removal of the organic constituents agreed with previous studies. The low removal of

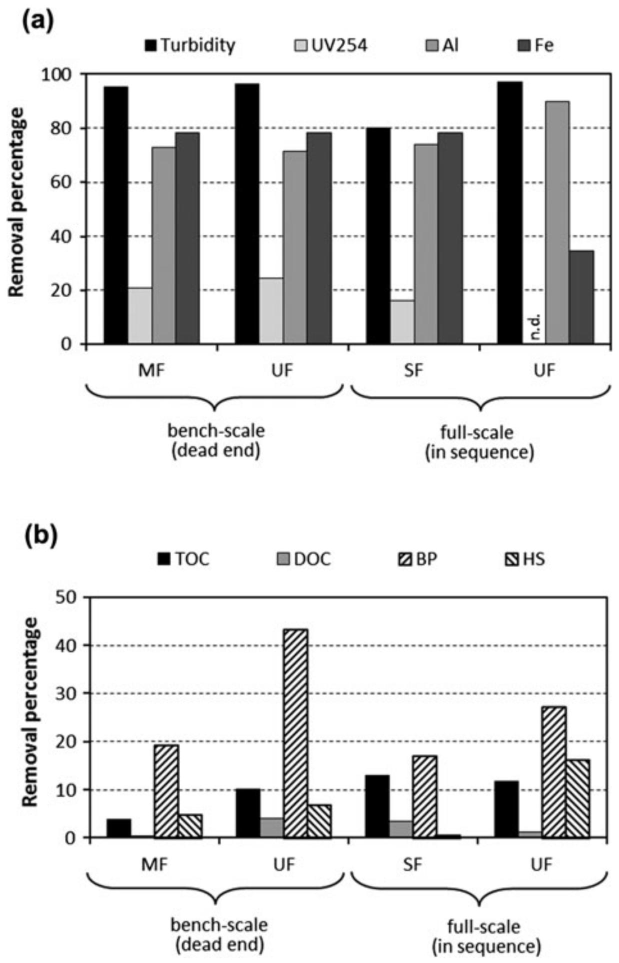

Fig. 4. Removal of (a) bulk parameters and inorganic ions and (b) organic parameters for MF_{bs} and UF_{bs} membranes under dead-end operation mode and for the SF + UF_{fs} sequence. Removals for UF_{fs} are referred to the feed decanted water (i.e. SF + UF_{fs}).
Note: n.d.: not determined.

DOC by UF_{bs} and MF_{bs} membranes agreed with Ye et al. [26] and Choi et al. [13], who reported DOC removals of 10–12%, respectively, under similar filtration conditions. The higher DOC removals reported by Choo and co-workers (17–24%) might be due, as pointed out by the authors, to the high concentration of Fe (up to 1.0 mg/l), which induced that "the material precipitated by oxidation (e.g. ferrihydrite) can play a part in removing NOM from water by sorption" [17]. Concerning the organic fractions, the finding of BP and to a minor degree HS as the only organic fractions retained by MF_{bs} and UF_{bs} (and thus identified as the major organic foulants), and their removal percentages, are also in agreement with other researchers [11,23,24,34]. Higher BP removals reported by other authors: 51–69% [21], 40–80% [12], 60% [26], 78–93% [25] and 57% [22] were likely due to the smaller pore sizes of their UF membranes (0.02–0.04 μm) that have might favoured the rejection of BP by sieving effects.

The removal mechanisms differed depending on the constituents removed. With regard to turbidity, the removal of particles smaller than the membrane pore size arriving at the early stages of a filtration cycle might occur initially by pore blocking (resulting in the initial sharp decrease in permeability of Fig. 3), while the removal of larger particles or additional small particles might occur by sieving effects and cake formation [4]. The removal of Fe and Al is likely due to precipitation in the form of (oxy)hydroxides. Again, Al- and Fe-(oxy)hydroxides larger than the MF_{bs} and UF_{bs} pores can accumulate on the membrane surface, leading to the cake formation, while smaller precipitates can block and narrow the pores of the membrane [1]. As reported by Pernitsky et al. [35], the theoretical solubility of Al under drinking water conditions is in the order of a few μg/L, clearly below the Al concentration in the decanted water used in the experiments, and therefore exceedance of their saturation limit is expected in the present experiments. Although to a lesser extent, complexation with organic matter to form insoluble complexes and/or complexes which are in turn retained by the UF membrane might be another mechanism for the Al and Fe removal [9,15,36,37].

As stated above, around 15% of the organic load was present in the form of particulate or colloidal OC. These organic particles were likely removed as for turbidity. The removal of dissolved BP and likely the highest MW portion of HS were interpreted to be due to size exclusion effects, resulting in the formation of a cake layer that in turn retains new arriving BP and HS. On the contrary, part of the smaller fractions (in particular HS) was likely adsorbed initially both inside the pores and on the membrane surface (resulting in pore blocking responsible for the initial steep decrease in permeability of Fig. 3) [12,22], and afterwards on already retained foulants in the cake layer [4,19,28]. Adsorption of DOC onto Al and Fe (oxy)hydroxides flocs has been reported to also play a role in the DOC removal [13,17]. Sieving as main mechanism of removal for highest MW organic fractions would explain why UF_{bs} always exhibited higher removals than MF_{bs}. In fact, the narrower pore size of UF_{bs} (0.08 μm) than of MF_{bs} (0.1 μm) (see Table 1) would retain more easily constituents larger than the size of the membrane pores, while water and constituents finer than pores would pass through the membrane to the filtrate side.

3.2.3. *Fouling composition and reversibility*

Based on the flow rates of feed and permeate streams, the experiment duration and the concentrations of the foulants considered, the masses of Al, Fe, BP and HS retained on the membrane were calculated through a mass balance. These masses are shown in Fig. 5.

The fouling layer on both MF_{bs} and UF_{bs} membranes appeared to be largely comprised of Al (with accumulated masses of 638 and 690 μg, respectively) and HS (with accumulated masses of 307 and 469 μg, respectively) along with smaller amounts of BP (93 and 229 μg, respectively) and Fe (64 and 71 μg, respectively). The higher amounts of foulants retained on the UF_{bs} membrane with respect to the MF_{bs} membrane were in accordance with the narrower pore size of the former.

The contribution of inorganic and organic constituents to MF and UF fouling has also been quantified by Howe and Clark [28] and Arnal et al. [29], who analysed the elemental composition of fouled membrane surface by SEM-EDX and found mass percentages in the range of 26–68% for C and 2–17% for Al depending on the quality of the feed water. They concluded that, in fact, both inorganic and organic components must be considered in an overall understanding of fouling.

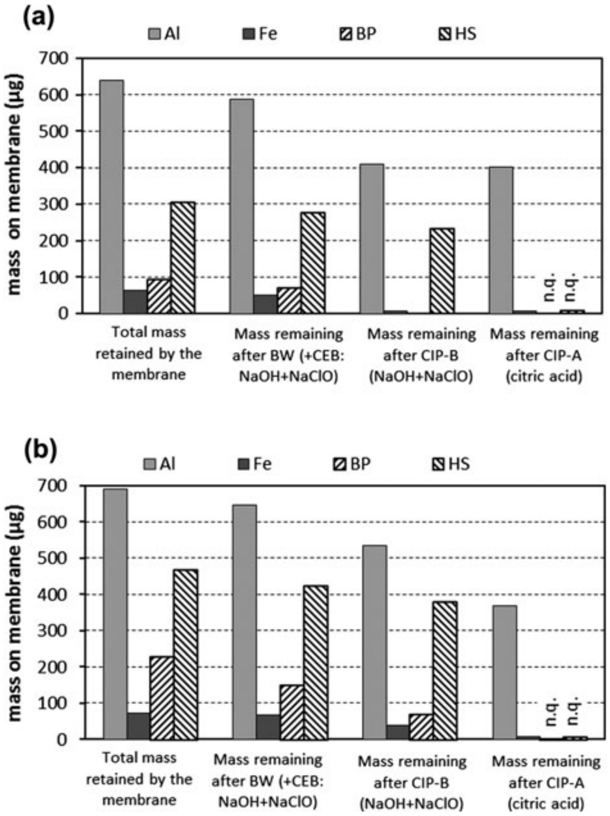

Fig. 5. Masses (in μg) of Al, Fe, BP and HS retained and remaining after the successive application of BW(+CEB: NaOH + NaClO), CIP-B (NaOH + NaClO), and CIP-A (citric acid) for the (a) MF_{bs} and (b) UF_{bs} membranes.
Note: n.q.: not quantifiable.

Reversibility of fouling was studied from foulant masses detached after each cleaning step, i.e. BW (+CEB), CIP-B and CIP-A. The detached masses were calculated through a mass balance considering the volume of each cleaning solution and its composition before and after applying it. The streams of the successive nine BW(+CEB) were collected into a separate tank as a composite sample. Therefore, the mass extracted by BW(+CEB) determined from the analysis of this composite sample refers to the mass extracted by all these nine BW(+CEB). Mass extracted by BW (+CEB), CIP-B and CIP-A were termed "BW-reversible fouling", "CIP-A-reversible fouling" and "CIP-B-reversible fouling". Fig. 5 shows the masses of foulant remaining on the membrane after each cleaning step for MF_{bs} (Fig. 5(a)) and UF_{bs} (Fig. 5(b)). Results showed that the fouling layer on both membranes exhibited fairly similar fouling reversibility behaviour.

Foulants were in general poorly washed out from the membranes by BW(+CEB), indicating that foulants were well adhered on/in the membrane, which agrees with the observed low membrane permeability recovery by BW(+CEB) in Fig. 3. BP were detached by 24% (for MF_{bs}) and 33% (for UF_{bs}), slightly more than Al (7–8%), Fe (7–19%) and HS (9%). These detachments by BW(+CEB) were accompanied, as discussed above in Section 3.2.1, by momentary recoveries of ca. 15–19% of the lost membrane permeability (Fig. 3). Which foulant caused most membrane hydraulic resistance could not be determined in this study because, as it has been reported, the amount of a given foulant on a membrane is not necessarily proportional to the hydraulic resistance it causes to the membrane [2]. Further studies are needed to elucidate the contribution of each foulant to the overall hydraulic resistance of the membrane.

The preferential washing out of the BP fraction was likely due to its size relative to that of the membrane pores: organic substances much larger than the membrane pores led to the formation of a cake weakly bound to the membrane and thus more readily washed out [21,22,26], while lighter fractions such as HS or microflocs of Al and Fe can cause pore blocking or build-up a denser and tight cake layer more closely adhered to the membrane surface and thus less readily detached from it by BW [14,16,20]. Differences between BW and BW(+CEB) were not appreciable, suggesting that fouling was removed by shear effects rather than by chemical reactions with NaClO and NaOH under CEB conditions. Consequently, there seems to be no need to apply any CEB under these filtration conditions, with the consequent lower reagent consumption and extension of membrane life.

The higher detachment of BP by BW than other organic fractions was in accordance with other studies [20,22]. Differences against other studies appear, however, in the percentage detachments. For instance, Wray et al. [21] reported a BP detachment from a UF membrane of 84–100%. Plausible reasons for this discrepancy were the different relative sizes between particles and membrane pore size that might have favoured fouling by the cake formation, which is more amenable to be washed out, and the more intensive BW regime (30 min of filtration and 10 min of BW) than the one applied in this study (20 min of filtration and only 1.0 min of BW).

CIP-B led to a larger detachment of foulants. For MF_{bs} a further 77, 69, 28 and 14% of the initial BP, Fe, Al and HS retained by the membrane were extracted by the NaOH + NaClO solution. For UF_{bs}, these percentages were 35, 41, 16 and 9%, respectively. The detachment of BP and HS fractions may be explained by the fact that organic compounds can be hydrolised at high pH and oxidised, increasing their solubility [8]. It must be noted that results for the detachment of organic matter shown in Fig. 5 must be considered with caution, because NaClO might have altered the proportion between organic fractions after oxidising organic molecules such as BP [18,20]. The detachment of Al and Fe was explained by the formation of soluble inorganic hydroxy-complexes (e.g. $Al(OH)_4^-$) and/or metal-NOM complexes [18].

Finally, the effect of applying the CIP-A solution resulted in the detachment of a further 1–11% of the initial Al and Fe, respectively, (for MF_{bs}) and 24–55% (for UF_{bs}). This detachment was due to the dissolution of Al– and Fe– precipitates by acid [8]. BP and HS detachment could not be quantified because the organic fractions detached, if any, might be in the HPSEC chromatograms overwhelmed by the very high concentration of citric acid employed as cleaning agent. However, it could be anticipated, according to Shi et al. [9] and Paugam et al. [38] that the acid cleaning step was not effective in cleaning BP. Large detachment of metals and low detachment of organic matter are in agreement with Kimura et al. [18].

Foulants remaining after CIP-A constituted the irreversible fouling. A percentage of 63 and 53% of the initial retained Al (for MF_{bs} and UF_{bs}, respectively) was found to remain after CIP-A, meaning that Al was a significant contributor to irreversible fouling. This is in accordance with Kimura et al. [18] and Arnal et al. [29]. On contrast, percentage of remaining Fe was <2% (for both MF_{bs} and UF_{bs}), meaning that Fe was completely removed from the MF_{bs} and UF_{bs} surface during CIP-A and did not contribute to irreversible fouling. This finding is in accordance with Arnal and co-workers, who found Al remaining on the membrane after the application of a number of acidic, basic and oxidising agents but not Fe [29]. As stated above, the final amounts of organic constituents remaining on the membrane could not be determined for analytical reasons associated to the HPSEC and therefore the irreversible organic fouling could not be quantified.

3.3. Comparison of MF_{bs} and UF_{bs} membranes against full-scale SF + UF_{fs} membrane

As shown also in Fig. 4, full-scale SF + UF_{fs} performed similarly to MF_{bs} and UF_{bs} in terms of removal of turbidity (97%), UV_{254} (17%), TOC (11%) and DOC (1%). SF + UF did yield higher removals of Al (90%) and HS (18%) and lower removals of Fe (overall removal 35%). BP were removed at a percentage (28%) between that of MF_{bs} and UF_{bs} (Fig. 4).

Looking at the removal in the successive SF + UF_{fs} units, it is worth noting that SF alone was capable of removing turbidity at levels (80%), UV_{254} (17%), Al (74%), Fe (78%), TOC (13%), DOC (3%) and BP (17%). These percentage removals were similar (for some constituents even higher) than MF_{bs} and UF_{bs}. This might seem surprising because a sand bed has a nominal pore size considerably greater than the MF and UF membrane pores. The reason of such good removal by SF lies on the height of the filtration bed and the tortuous path for the water as it flows down through the sand bed [39]. It is this approx. 20% remaining Al in the sand-filtered water that makes necessary the in-line coagulation before UF_{fs}. Further UF_{fs} enhanced the removal of turbidity (97%), Al (90%) and BP (28%), leaving the contents of the other components (TOC, DOC, HS) practically unaltered except Fe, whose removal was lowered to 35%. In the view of the results, the in-line coagulation serves indeed to successfully remove Al at expenses of adding Fe.

The higher overall removal of Al and BP by UF_{fs} compared to MF_{bs} and UF_{bs} is explained by: (1) the in-line coagulation, whereby Al and BP are entrapped within and adsorbed onto Fe-flocs during filtration and (2) its narrower pore size (0.02 μm), which favours the removal of constituents by size-exclusion effects. Surprisingly, and contradicting the above explanation, BP were better removed by UF_{bs} than UF_{fs}. The reason behind this apparent contradiction lies on the fact that solute removal does not depend only on the relative size between the solute and the pore size of the membrane (i.e. size exclusion effects) but also on the hydrophobicity/hydrophilicity and the surface charge of the membrane [2,40]. In general, the more hydrophobic a membrane material is, the more affinity it exhibits toward hydrophobic solutes. Also, the stronger the electrostatic interaction occurring between a charged membrane material and a charged solute, the higher the attraction (if the charges have opposite sign) or repulsion (if the charges have the same sign). The hydrophobicity and surface charge of a membrane can be inferred by the contact angle and zeta potential measurements, respectively [2,40]. As shown in Table 1, UF_{bs} and UF_{fs} differed not only in pore size but also in the membrane material (PS for UF_{bs} and PVDF for UF_{fs}). Neither the contact angle nor the zeta potential could be measured in this study. However, PS membranes are generally more hydrophobic than PVDF ones, with corresponding contact angles typically in the range of 60°–70° and 40°–50°, respectively, (although these ranges must be taken as indicative only because the contact angle value may vary due to surface chemistry modifications, the roughness of the material and even the techniques used by individual investigators) [41]. BP, which are mainly constituted by polysaccharides, polypeptides, proteins and amino sugars (see Section 2.4) tend to exhibit a hydrophobic character and be uncharged, showing thus a higher affinity towards PS than towards PVDF membranes. This fact could explain why BP were more retained by UF_{bs} than by UF_{fs}. Differences in DOC removals attributed to membrane material properties (and against what would be expected from their MWCO) have also been reported by previous researchers [2,42]. Moreover, the operation mode (i.e. filtration under constant pressure or constant flux conditions) and the flux value may also influence the extent of solute removal and thus fouling [43]. Sim et al. reported that, under constant flux conditions, fouling potential decreased when flux was decreased [43]. The fact that the UF_{fs} operated at lower fluxes (0.012 L/(s m^2)) than MF_{bs} and UF_{bs} (0.030 L/(s m^2)) might have contributed to the lower retention of BP by UF_{fs}.

3.4. Performance of MF_{bs} and UF_{bs} membranes under cross-flow operation mode

The permeability decline for MF_{bs} and UF_{bs} under cross-flow conditions (Fig. 6) approached the one observed under dead-end conditions (Fig. 3). Again, MF_{bs} suffered from less permeability loss than UF_{bs}, with P/P_0 levelling off at 0.5 for the former and at 0.4 for the latter. Also similarly to what was observed under dead-end conditions, BW(+CEB) restored only a fraction of the permeability loss (physically irreversible fouling), and only when CIP was applied was the permeability restored.

It was observed, however, that permeability at the end of each filtration cycle was kept higher under cross-flow than under dead-end for both MF_{bs} (on average 8% higher) and UF_{bs} (on average 9% higher). This finding is explained by the cross-flow configuration itself: the flow parallel to the membrane surface not permeated (i.e. the retentate) provides a constant shear force that flushes foulants retained by the membrane. This flushing of foulants translates into a retardation of the membrane fouling and, thus, a less severe permeability decline. These results are qualitatively in accordance with Shamsuddin et al. [7], who compared dead-end and cross-flow operation modes and observed that permeability of the latter was approx. twice that of the former. It is also to note that cross-flow velocity was very similar for both MF_{bs} and UF_{bs} membranes (0.0018–0.0019 m/s, respectively) and therefore any possible effect of cross-flow velocity on specific cake resistance on the membrane surfaces [43] could be expected to be negligible.

Percentage removals of water constituents were similar for MF_{bs} and UF_{bs} under cross-flow operation mode: 92–97% for turbidity, 59% for Al and 2–5% for TOC. Fe in permeate was found below detection limit (5 µg/L) and its removal percentage could not be specified beyond >67% (Fig. 7).

In comparison to dead-end operation mode, it was found that turbidity was equally removed for both operation modes, while for the rest of components

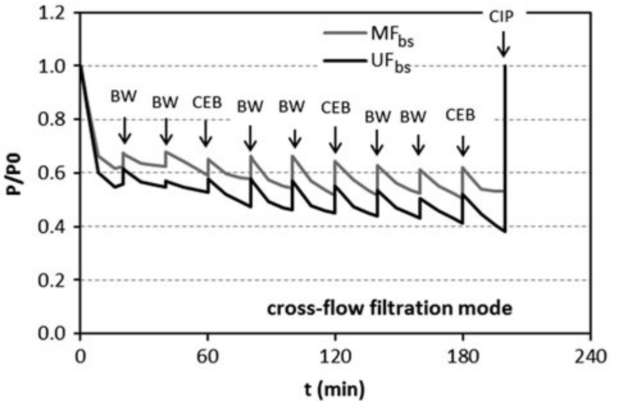

Fig. 6. Evolution of normalised permeability (P/P_0) for MF_{bs} and UF_{bs} membranes operated under cross-flow filtration mode.

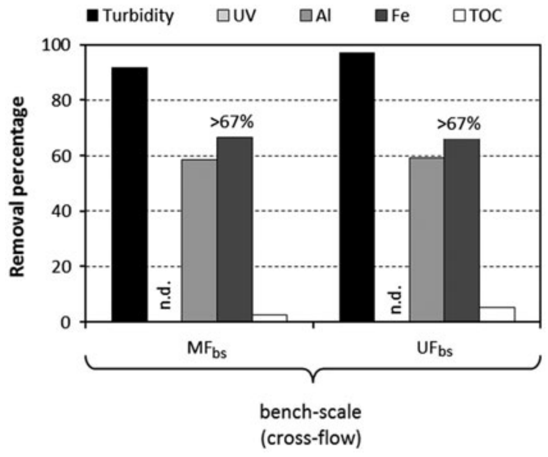

Fig. 7. Removal of organic and inorganic components for MF_{bs} and UF_{bs} membranes under cross-flow operation. Note: n.d.: not determined.

determined (Al and TOC) removals were lower for cross-flow than for dead-end (20% lower for Al and 50% lower for TOC). The higher removal of Al and TOC was due to the higher accumulation of foulants on the surface, which translates into losses of membrane permeability but also to a more effective retention of constituents by sieving and adsorption mechanisms by the foulant layer.

Further research is needed to determine whether the benefit of this 8–9% increase in permeability provided by the cross-flow operation mode compensates the low conversion ratio of 66%, the expected higher energy consumption per volume of produced water and the slightly impoverished quality of the produced water compared to that of the dead-end mode.

4. Conclusions

Based on the results of this study, several conclusions can be drawn as follows:

(1) Both MF_{bs} and UF_{bs} membranes successfully removed turbidity, Al and Fe (by >70%), whereas UV_{254} was moderately removed (20–25%) and TOC and DOC poorly removed (<10%). With regard to the organic fractions, the percentage removals were 19–43% for BP and 5–7% for HS. Phosphorous and the smallest organic fractions (BB, LMWN and LMWA) seemed to totally permeate through both MF_{bs} and UF_{bs}. UF_{bs} clearly performed better than MF_{bs} in removing organic matter and its fractions, but also suffered more flux decline (10% more).

(2) For both MF_{bs} and UF_{bs}, fouling was mainly comprised by Al and HS (mass percentages of 58–47 and 28–32%, respectively), with minor amounts of BP and Fe (8–16 and 6–5%, respectively).

(3) Foulants were in general poorly washed out from the MF_{bs} and UF_{bs} membranes by BW (mostly <10%) except BP, which was detached by 24–33%. The limited detachment of foulants when a BW was applied was accompanied by a slight and momentary increase of the membrane permeability.

(4) CIP-B consisting in soaking the membrane in a NaOH + NaClO solution led to a larger detachment of foulants from the MF_{bs} and UF_{bs} membranes: 77–35% of the intial BP, 28–16% of Al, 69–41% of Fe, and 14–9% of HS.

(5) CIP-A consisting in soaking the membrane in a citric acid solution (pH 3–4) resulted in the detachment of a further 1–24 and 24–55% of initial Al and Fe, respectively. BP and HS detachment could not be quantified by HPSEC due to analytical limitations posed by the presence of the citric acid.

(6) Compared with the bench scale MF_{bs} and UF_{bs}, full-scale SF + UF_{fs} yielded similar removal of turbidity removals, but higher removals of Al (90%) and HS (18%) and lower removals of Fe (overall removal 35%). BP were removed at a percentage (28%) between that of MF_{bs} and UF_{bs}. The higher BP removal by UF_{bs} than by UF_{fs} despite having a higher pore size is attributed to the fact that the UF_{bs} membrane is made of PS, which exhibited a more hydrophobic character and thus a more affinity towards hydrophobic BP. Hence, UF_{bs} appears, in terms of quality of the produced water, a feasible option for replacing SF + UF_{fs} of the DWTP in Sant Joan Despí.

(7) Permeability at the end of each filtration cycle was kept higher under cross-flow than under dead-end conditions for both MF_{bs} (on average 8% higher) and UF_{bs} (on average 9% higher). However, while the removal of turbidity was similar for both operation modes, Al and TOC removals were lower for the former than for the latter (20% lower for Al and 50% lower for TOC).

Acknowledgements

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Abbreviations

BB	—	building blocks
BP	—	biopolymers
BW	—	backwash
CEB	—	chemically enhanced backwash
CIP	—	cleaning-in-place
CIP-A	—	acidic CIP
CIP-B	—	basic CIP
DOC	—	dissolved organic carbon
DWTP	—	drinking water treatment plant
FEEM	—	fluorescence excitation-emission matrix
HPSEC	—	high-performance size exclusion chromatography
HS	—	humic substances
LMWA	—	low molecular weight acids
LMWN	—	low molecular weight neutrals
MF	—	microfiltration
MF_{bs}	—	bench-scale MF
MW	—	molecular weight
MWCO	—	molecular weight cut-off
NOM	—	natural organic matter
PS	—	polysulfone
PVDF	—	polyvinylidene difluoride
RO	—	reverse osmosis
SF	—	sand filtration
SUVA	—	specific absorbance at 254 nm
TMP	—	transmembrane pressure
TOC	—	total organic carbon
UF	—	ultrafiltration
UF_{bs}	—	bench-scale UF
UF_{fs}	—	full-scale UF
UV_{254}	—	absorbance at 254 nm

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