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Reversibility of fouling on ultrafiltration membrane by backwashing and chemical cleaning: differences in organic fractions behaviour

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ABSTRACT

Membrane fouling is an inherent phenomenon in ultrafiltration (UF) membrane processes, making it necessary to periodically perform backwashes (BW) and chemical "cleanings in place" (CIP) to restore the initial permeability of the membrane. The objective of this study was (1) to explore systematically the effect of distinct BW-related variables (BW transmembrane pressure, duration, frequency and composition) on the reversibility of UF membrane fouling and on the permeate quality (in terms of total organic carbon, turbidity and UV absorbance) over successive filtration/BW cycles; and (2) to identify which organic fractions were most removed by the membrane and, of these, which were most detached after BW, alkaline and oxidant CIP and acid CIP episodes. For this purpose, a bench-scale outside-in hollow fibre module operated under dead-end filtration mode at constant transmembrane pressure and treating settled water from a drinking water treatment plant was employed. Dissolved organic carbon fractionation was performed by high-performance size-exclusion chromatography. Results showed that, in general, the more intensive the BW was (in terms of high transmembrane pressure, shortened frequency and prolonged duration) the more effective it was in removing fouling from the membrane. Concerning the composition of the water used for the BW, the addition of NaClO led to maximum fouling reversibility, closely followed by the combination of NaOH + NaClO, while citric acid and NaOH contributed little compared to water alone. However, results also showed that irreversible fouling was never completely avoided whatever the BW regime applied, leading to a gradual increase in the total resistance over time. Larger differences in the behaviour of the different organic fractions were observed. UF membrane preferentially retained the heaviest fraction of biopolymers (BP), while the intermediate fraction of humic substances (HS) was removed at a lower percentage and the lighter fractions seemed to entirely pass through the UF membrane. The successive application of BW and CIPs resulted in the detachment from the membrane of a significant percentage of the retained BP, whereas only a modest percentage of the retained HS.

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

1. Introduction

Application of pressure-driven membrane processes as microfiltration (MF) and ultrafiltration (UF) has expanded in recent years as an alternative technology for wastewater treatment and drinking water production. This expansion is due to the fact that UF has proved to be an effective physical barrier to particles, colloids, bacteria and certain viruses that are larger than the UF membrane pores and, hence, are retained by size-exclusion mechanisms, among others. Furthermore, UF provides extra advantages over conventional treatments such as small footprint, low energy consumption, limited chemical dosing, capability of coping with wide fluctuations in feed quality and delivering permeate of relatively constant quality, and reduced scale-up risks [1–5].

The retained particles accumulated on the feed side of the membrane (and within the membrane pores), however, give rise to the major drawback of UF systems: fouling formation. Fouling leads to additional hydraulic resistance to permeate flow, increase in the energy consumption of the process, lowering of the productivity, worsening of the product quality and eventually premature replacement of membranes [2,4,6–8].

In order to remove fouling, UF membranes are periodically subjected to physical cleaning such as backwashing (BW). BW is performed by reversing the direction of flow through the membrane to dislodge and remove foulants from it and restore the initial permeability [6,8–10]. Fouling removed by a hydraulic cleaning such as BW is referred to as “physically reversible fouling”, in opposition to the “irreversible fouling” made of substances strongly adhered on or within the membrane and not flushed out by any physical cleaning procedure. It is this irreversible fouling that leads to a long-term increase in the resistance (with the subsequent increase in the operational costs) and to a progressive deterioration of the membrane.

The operation of a UF membrane consists, then, of a succession of cycles each comprising a filtration step (in which membrane resistance gradually increases due to fouling) and a BW step (in which membrane resistance is lowered as foulants are removed from the membrane). Fig. 1 schematically represents the evolution of the total membrane resistance during its operation, showing all its components, i.e. resistance of clean membrane (R_m), resistance due to the reversible fouling (R_rev) and resistance due to the irreversible fouling (R_irrev).

The removal of the irreversible fouling can be partially achieved only through aggressive chemical cleaning (“cleaning in place” (CIP)), which is usually burdensome and requires the shutdown of the unit being cleaned for several hours. Chemical cleaning causes both a reduction of the overall production plant capacity and a deterioration of the membranes, wherefore it should be minimised wherever possible [3,11]. A strategy that helps minimise chemical cleaning is the addition of chemical cleaners into the water used for BW, giving rise to the so-called “chemically-enhanced backwash” (CEB) [12]. This cleaning operation does not require an extended shutdown, since it is conducted on line, and the chemicals’ concentration and/or their nature tend to be less aggressive compared to the CIP ones. As a consequence, typically CEBs are less effective than CIPs.

The extent and reversibility of membrane fouling are largely dependent on multiple variables, such as membrane characteristics, feed water properties, filtration conditions, module configuration, BW regime, etc., making the control of membrane fouling a complex phenomenon. Among these, the effect of feed water composition and membrane operating conditions has been most researched [8,13–15], while less studies have dealt with the effect that BW variables (duration, frequency, etc.) or different organic components of the dissolved organic matter (DOM) exert on UF membrane fouling.

Comparison of results from studies on BW variables is, moreover, not entirely reliable and needs to be treated with caution for several reasons. First, these studies treat different types of water: wastewater [2,5,6,11,12,16], seawater [1,17,18] and surface water [3,10], each with different fouling behaviour potentials under a given BW regime. For instance, it has been reported that a high salt concentration in the seawater might influence the interaction forces between membrane and foulants [1]. Second, the configuration of UF modules in these studies is very variable: flat-sheet [10], spiral wound [17], pressurised (inside-out) [5,6,12,18] and submerged (outside-in) [1,10] hollow fibre membrane systems also affecting the propensity to fouling [1,16,19]. Furthermore, most of them are focused on the evolution of the membrane resistance and fouling rates [2,3,5,6,16] and only a few quantify

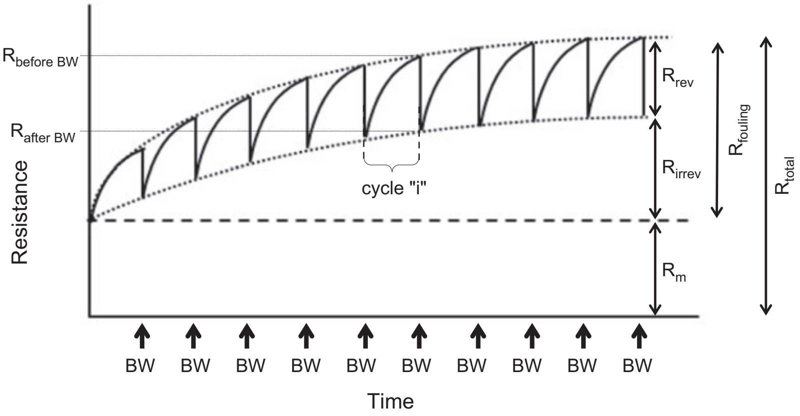

Fig. 1. Qualitative representation of the evolution of membrane resistance over a succession of filtration and BW cycles.

the reversible and irreversible fouling after each backwash cycle [1]. Within this context, more research is still needed on quantitatively determining the effect of BW-related variables on the reversibility of fouling on UF membranes for all scenarios and, in particular, for the outside-in hollow fibre UF for surface water.

Fouling by DOM components or fractions is also gaining increasing attention of researchers. Indeed, it is acknowledged that different constituents of DOM do not necessarily foul UF membranes on the same way or degree [20–22]. Characterising such DOM fractions is, thus, essential for a better understanding of which constituents contribute most in the fouling of a UF membrane. Among the methods developed to characterise DOM, high-performance size-exclusion chromatography (HPSEC), whereby dissolved organic carbon (DOC) fractions are separated according to their hydrodynamic size, has gained much attention as a powerful method for quantitative and qualitative characterisation of DOC [23].

The objective of this study was (1) to explore systematically the effect of distinct BW-related variables on the reversibility of UF membrane fouling and on the permeate quality over successive filtration/BW cycles in the treatment of surface water; and (2) to identify which organic fractions were best removed after BW and cleaning-in-place (CIP) episodes. For this purpose, a bench-scale outside-in hollow fibre module operated under dead-end filtration mode at constant transmembrane pressure (TMP) was employed. The variables of study comprised BW, TMP, duration and frequency as well as composition of CEBs. Permeate quality was monitored in terms of total organic carbon (TOC), turbidity and UV absorbance (UV_{254}). For the second objective, DOC fractionation was performed by HPSEC.

2. Methods

2.1. Feed water characteristics

The feed water to be filtered by the UF module was decanted water from the settling basin of the drinking water treatment plant in Sant Joan Despí (Barcelona, Spain). The average composition of this water during the course of the study is given in Table 1.

2.2. UF device and membrane characteristics

All experiments conducted in this study were carried out employing a bench-scale outside-in hollow fibre module (Polymem UF0808M3) operated under dead-end filtration mode at constant TMP. The main characteristics of the UF module provided by the manufacturer are shown in Table 2.

The decanted feed water was directed to the UF module by means of a centrifugal pump (IML S.A.U.,

Table 1
Average feed water quality. Confidence intervals at a confidence level of 95% for all cases. Number of analysed samples: 75 (for pH, conductivity, turbidity and Abs_{254}) and 14 (for TOC, Al, Fe and P)

Parameter	Concentration
pH	7.6 ± 0.1
Conductivity (µS cm^{-1})	1,490 ± 160
Turbidity (NTU)	1.76 ± 0.19
Abs_{254} (abs m^{-1})	0.080 ± 0.006
TOC (mg L^{-1})	4.1 ± 0.24
Al (µg L^{-1})	364 ± 51
Fe (µg L^{-1})	23 ± 9
P (µg L^{-1})	43 ± 14

Table 2
Characteristics of the UF membrane module provided by the manufacturer

Manufacturer	Polymem
Membrane type	UF0808M3
Filtration mode	Out-in
Membrane material	Polysulfone
Potting material	Polyurethane
Vessel material	U-PVC
Fibre diameter (mm)	1.4
Surface area (m)	0.01
Module external diameter (mm)	20
Module length (mm)	200
Nominal MWCO (Da)	300,000
Nominal pore size (μm)	0.08
Maximum feeding pressure (bar)	3.0
Maximum TMP (bar)	1.5
Maximum TMP during backwash (bar)	2.0
Maximum temperature (°C)	35
pH range	2–12

Model MS100 M). Valves in the system were opened and closed such that the direction of flow was out-in during the filtration step and reversed to in-out during the BW step. During filtration, the feed solution passed through the UF membrane and permeate was collected for flux measurements and chemical analysis. TMP was measured by a pressure gauge (Keller Group, model Leo 3). BW was carried out with UF permeate by temporarily reversing flow using a peristaltic pump (Heidolph, model Pump drive PD5001), and the BW stream was discharged into a separate tank. A schematic diagram of the experimental set-up is shown in Fig. 2.

2.3. Filtration procedure

Prior to each fouling experiment, the cleaned membrane resistance (R_m) was measured through a filtration test with deionised water. These tests were conducted in dead-end mode at a TMP of 1.2 bar without recirculation of permeate for 15 min and then with recirculation until constant permeate production. At this point, R_m was calculated according to the well-established Darcy's equation described in Section 2.6.

Each filtration experiment was carried out at a filtration TMP of 1.2 bar and one combination of BW-related variables, i.e. backwash Transmembrane pressure (BW_{TMP}), backwash duration (BW_d), backwash frequency (BW_f) and CEB composition ($BW_{CEB\text{-}c}$). For the carrying out of the experiments with CEBs, the dose of NaClO was 7 mg/L (as active Cl), while NaOH and citric acid were added to bring pH to 10–11 and to 3–4, respectively. In order to isolate the effect of these variables on fouling reversibility, each of them was varied (as shown in Table 3), while setting all other variables at fixed values (marked in bold in Table 3). In order to ensure consistency of results, each filtration experiment was conducted in duplicate (except those of the $BW_{CEB\text{-}c}$ set evaluating NaClO, NaOH and citric acid, which were performed only once), giving rise to a total number of 23 experiments.

Permeate flux and quality were monitored all over each filtration experiment, which lasted 200 min. This duration encompassed a number of filtration cycles large enough for results to be statistically significant. Flux was measured by the timed collection of permeate in a volumetric flask. Because feed water for all

Table 3
Summary of the experimental conditions and variation of each set of experiments conducted during the study

Variable of study	Tested values
BW_{TMP} (bar)	0.7, 1.0, 1.5, **1.8**
BW_f (min)	10, **20**, 40, 60
BW_d (min)	0.5, **1.0**, 2.0
$BW_{CEB\text{-}c}$	**Blank***, NaClO, NaOH, NaOH+NaClO, citric acid

Note: *Blank means BW with UF permeate. The pre-fixed value is marked in bold.

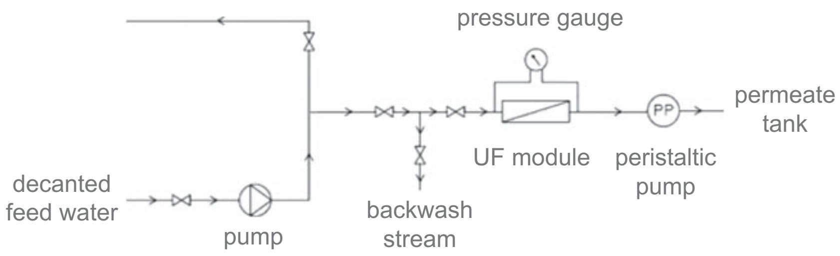

Fig. 2. Schematic diagram of the experimental UF system set-up.

experiments was taken from the same location in the treatment train of the drinking water treatment plant in Sant Joan Despí, the differences observed in fouling reversibility could be attributed to the investigated BW-related variables.

2.4. Removal and reversibility of organic fractions

Further efforts were devoted to investigate which organic fractions were most removed by the UF membrane and which were most detached from it after the successive application of BW (assisted with intermittent CEB), a CIP based on alkaline and oxidant agents (CIP-B) and finally, a CIP based on an acid agent (CIP-A). This allowed quantify the reversible fouling after each BW and cleaning step and eventually the irreversible fouling on the UF membrane.

For this purpose, a filtration experiment was conducted similarly to those described above at a constant TMP of 1.2 bar and a BW regime optimised from the previous set of experiments, i.e. BW was performed every 20 min of filtration at a TMP of 1.8 bar and with a duration of 1.0 min. Additional CEBs based on a combination of NaClO (7 mg/L) and NaOH (pH 10–11) were applied every three BW. A total volume of 3.945 L of feed water was filtered, of which 0.337 L was used for BW. On completion of the filtration experiment, the UF membrane was consecutively subjected first to the CIP-B with the addition of NaOH (pH between 11 and 12) in combination with 200 mg/L NaClO (volume 50 mL, contact time 90 min) and, second, to the CIP-A with the addition of citric acid (pH between 3 and 4, volume 50 mL and contact time 30 min). The reagents used for CIP-B and CIP-A were selected in accordance with the ones used in the drinking water treatment plant of Sant Joan Despí.

Feed and permeate over the experiment were collected for analysis of DOC and its fractions (see below analytical techniques) by HPSEC. Organic fractionation was also performed for the successive BW streams (collected as a composite sample) and CIP-B and CIP-A solutions.

2.5. Chemical analysis of water samples

Feed water and UF permeate quality for the first set of experiments was analysed in terms of turbidity, TOC and UV_{254}. The samples were collected in sterile vials and stored in cold conditions until analysis in the laboratory. Turbidity was analysed by nephelometry (Hach 2100 AN IS Turbidimeter), absorbance was analysed by spectrophotometry (Hach DR 5000) and TOC by oxidative combustion and infrared detection (Shimadzu V CPH).

Fractionation of DOC was performed by HPSEC using a Toyopearl TSK HW-50S column (250 × 20 mm) coupled to on-line UV254, organic carbon (OC) and organic nitrogen detectors by DOC-Labor (Karlsruhe). The principles of the technique are reported in depth by Huber et al. [23]. Briefly, it is based on size-exclusion liquid chromatography whereby organic compounds are fractionated into five sub-fractions according to their molecular weight (MW): (1) biopolymers (BP, with MW > 20,000 g/mol, basically constituted by polysaccharides and proteins); (2) humic substances (HS, with MW of approx. 1,000 g/mol, constituted by fulvic and humic acids); (3) building blocks (BB, with MW between 300 and 500 g/mol, constituted by breakdown products of humics); (4) low molecular weight acids (LMWA, with MW < 350 g/mol, constituted by alcohols, aldehydes, ketones, sugars and amino acids); and (5) low molecular neutrals (LMWN, with MW < 350 g/mol, constituted by alcohols, aldehydes, ketones and amino acids). The OC retained in the chromatographic column (i.e. non-chromatographic DOC) is termed as hydrophobic fraction. Based on the differences in UV-active components or nitrogen content, HPSEC can also determine the content of proteins within the BP fraction.

2.6. Data treatment for the membrane hydraulic performance evaluation

Fouling was determined by the increase in resistance posed by the fouled membrane, which in turn calculated from the decline of permeate flux according to the well-established Darcy's equation:

$$J = \frac{\Delta P}{\mu \cdot R_{\text{total}}} \tag{1}$$

where J is the permeate flux ($m^3 m^{-2} s^{-1}$), ΔP is the TMP (bar), μ is the permeate viscosity (bars) (corrected to 20˚C) and R_{total} is the total resistance of the fouled membrane (m^{-1}). According to Darcy's law, a decrease in J under constant ΔP during membrane filtration process (or equivalently an increase in ΔP under constant J) is indicative of membrane fouling. The total resistance can be described by the resistance-in-series model and expressed as [4,10,13]:

$$J = \frac{\Delta P}{\mu \cdot (R_{\text{m}} + R_{\text{rev}} + R_{\text{irrev}})} \tag{2}$$

where R_{m} is the cleaned membrane resistance (measured before each experiment with deionised water), and R_{rev} and R_{irrev} are the hydraulically reversible and irreversible fouling resistances, respectively.

For each filtration cycle "i" $R^{\mathrm{i}}_{\mathrm{rev}}$ was calculated as the difference of resistance measured before and after BW (as shown in Fig. 2).

$$R^{\mathrm{i}}_{\mathrm{rev}} = R^{\mathrm{i}}_{\mathrm{before\,BW}} - R^{\mathrm{i}}_{\mathrm{after\,BW}} \tag{3}$$

The contribution of $R^{\mathrm{i}}_{\mathrm{rev}}$ over the total fouling of the membrane (R_{fouling}) can then be calculated as follows (see Fig. 1):

$$\text{Reversible fouling}\,(\%) = \frac{R^{\mathrm{i}}_{\mathrm{rev}}}{R^{\mathrm{i}}_{\mathrm{fouling}}} = \frac{R^{\mathrm{i}}_{\mathrm{before\,BW}} - R^{\mathrm{i}}_{\mathrm{after\,BW}}}{R^{\mathrm{i}}_{\mathrm{before\,BW}} - R_{\mathrm{m}}} \tag{4}$$

In this study, averaged reversible fouling percentages over all filtration cycles and duplicates under the same experimental conditions are reported for comparison between different BW regimes.

It must be remarked here that most published studies report experimental data on a dimensionless basis (e.g. normalised flux, pressure, permeability or resistance). While this facilitates indeed comparison of experiments carried out under different experimental conditions, it also masks the possible effects of initial fouling on fouling evolution. For this reason, measured fouling-related variables were not normalised and reported as measured.

3. Results

Plotted in Figs. 3–6 are: (a) the total resistance curves obtained for each set of BW conditions, (b) the degree of membrane fouling reversibility calculated from the resistance profile and according to Eq. 2 and (c) the quality of permeate in terms of turbidity, UV_{254} and TOC. In all cases, resistance profile showed a pattern as described in Fig. 1, i.e. an increase in resistance during the filtration step and a decrease during BW. The resistance was, however, not completely restored to the initial value, indicating that, regardless of the BW regime, irreversible foulants slowly accumulated onto and into the membrane.

3.1. *Effect of backwashing transmembrane pressure (BW_{TMP})*

As shown in Fig. 3, higher $\mathrm{BW}_{\mathrm{TMP}}$ provided a lower resistance increase (i.e. a better permeability restoration) over the experiment (Fig. 3(a)) and a higher degree of fouling reversibility (Fig. 3(b)). R_{rev} percentage was below 30% at $\mathrm{BW}_{\mathrm{TMP}}$ of 0.7 and 1.0 bar, but it increased to 31% at $\mathrm{BW}_{\mathrm{TMP}}$ of 1.5 bar and up to 41% at $\mathrm{BW}_{\mathrm{TMP}}$ of 1.8 bar. This trend is likely due to the fact that shearing stress can more efficiently wash out tightly bound foulants from the membrane that would not be removed by lower $\mathrm{BW}_{\mathrm{TMP}}$.

This finding is partially in accordance with that reported by Remize et al. [10], who observed that increasing $\mathrm{BW}_{\mathrm{TMP}}$ from 1.2–2.0 bar in the filtration of surface water with UF membranes resulted in an increase in the foulants removed from the membrane (from 25 to 44%). Interestingly, and in opposition to our study, this trend did not translate into an increase in permeability recovery with $\mathrm{BW}_{\mathrm{TMP}}$, highlighting that measurement of permeability (or resistance) recovery may not be sufficient to identify fouling removal and that measurement of matter removed may be also necessary.

With regard to the permeate quality, removal of turbidity, UV_{254} and TOC were comparable within the experimental error whatever the $\mathrm{BW}_{\mathrm{TMP}}$ applied (Fig. 3(c)). Turbidity was decreased at a high degree (average removals of 89%), while Abs_{254} and TOC were decreased by 20 and 5% for all $\mathrm{BW}_{\mathrm{TMP}}$ values. The low retention of TOC by the UF membrane may be explained by the predominance in the decanted water of small molecular weight (MW) organic fractions with $\mathrm{MW} \leq 1{,}000$ Da (see Section 3.5), much smaller than the nominal MWCO of the UF membrane (300,000 Da, see Table 2).

3.2. *Effect of BW frequency (BW_f)*

The effect of BW_{f} on the total resistance, fouling reversibility and permeate quality during the process of membrane filtration is shown in Fig. 4. It is noticeable in Fig. 4(a) that the initial resistance for $\mathrm{BW}_{\mathrm{f}} = 10$ min was slightly higher than that corresponding for all other BW_{f}, suggesting that permeability membrane before that experiment had not been completely restored. Even so, BW every 10 min resulted in a lower fouling rate, in contrast to BW at stretched frequencies (20, 40 and 60 min), which led to a more severe increase in fouling resistance (i.e. accumulation of irreversible fouling) during membrane operation. As shown in Fig. 4(b), the more frequent the BW, the higher the reversibility of fouling: fouling reversibility decreased from 50% for BW_{f} of 10 min to 41% for BW_{f} of 20 min and below 37% for both BW_{f} of 40 and 60 min.

Similar trends on lowered fouling accumulation with more frequent BW have been reported by other researchers, although the degree of dependence differs considerably if other types of feed water or UF configurations are used as it is commonly the case

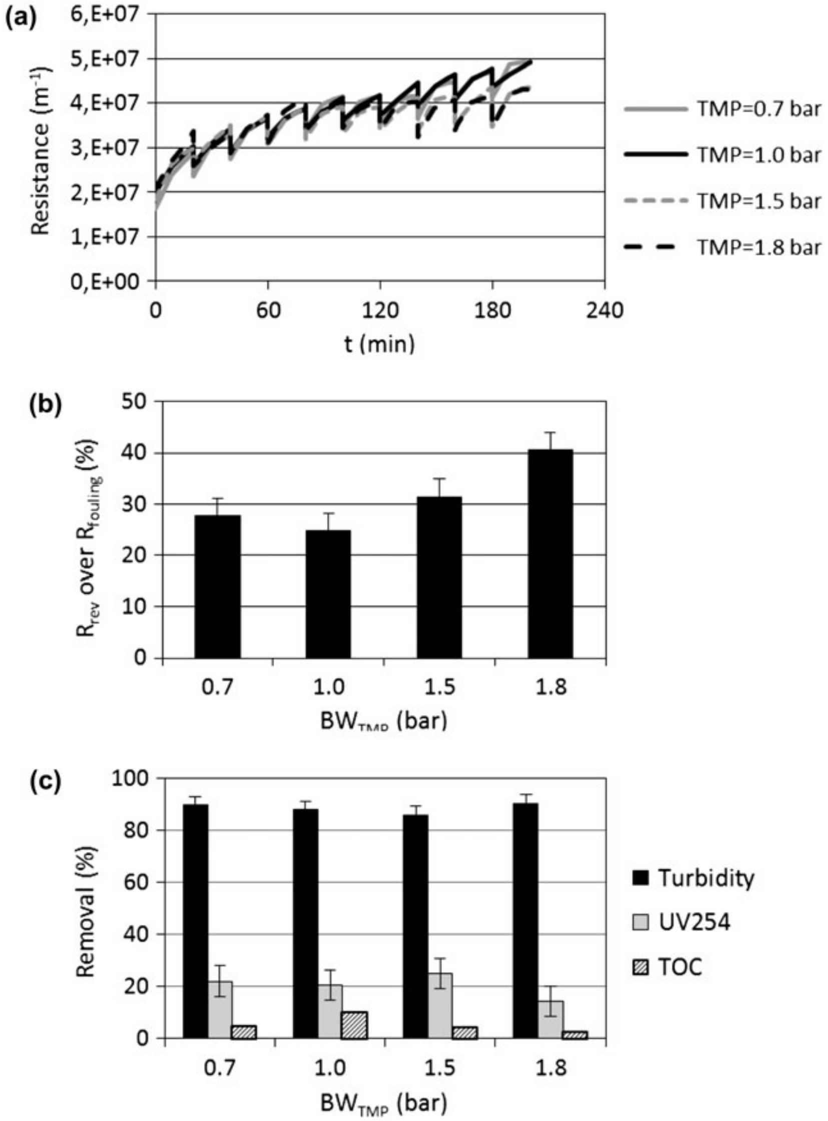

Fig. 3. Effect of backwash transmembrane pressure (BW_{TMP}) on the (a) total resistance of the fouled membrane, (b) percentage of reversible fouling over the total membrane fouling, and (c) removal of turbidity, UV_{254} and TOC by the UF membrane. Error bars correspond to confidence intervals at a confidence level of 95% for all cases.

[2,5,12]. There is, however, consensus that stretched BW frequencies allow more material to be accumulated on the membrane surface during a filtration cycle, forming a fouling layer more tightly attached and compacted and exhibiting, thus, a lower degree of reversibility under a given BW [1,6,16].

Concerning the permeate quality, no significant differences were observed neither under the different BW_f tested nor compared with the previous set of experiments under different BW_{TMP}. Turbidity removal was 91%, whereas those of UV_{254} and TOC were only 15 and 5%, respectively.

3.3. Effect of BW duration (BW_d)

The effect of BW_d on the total resistance, fouling reversibility and permeate quality during the process of membrane filtration is shown in Fig. 5. As in the previous set of experiments, an experiment showed an initial membrane resistance slightly higher than that corresponding to the other experiments, suggesting again that the membrane was not completely cleaned prior to the filtration experiment. Despite the different starting points, the evolution of resistance for over all experiments is comparable.

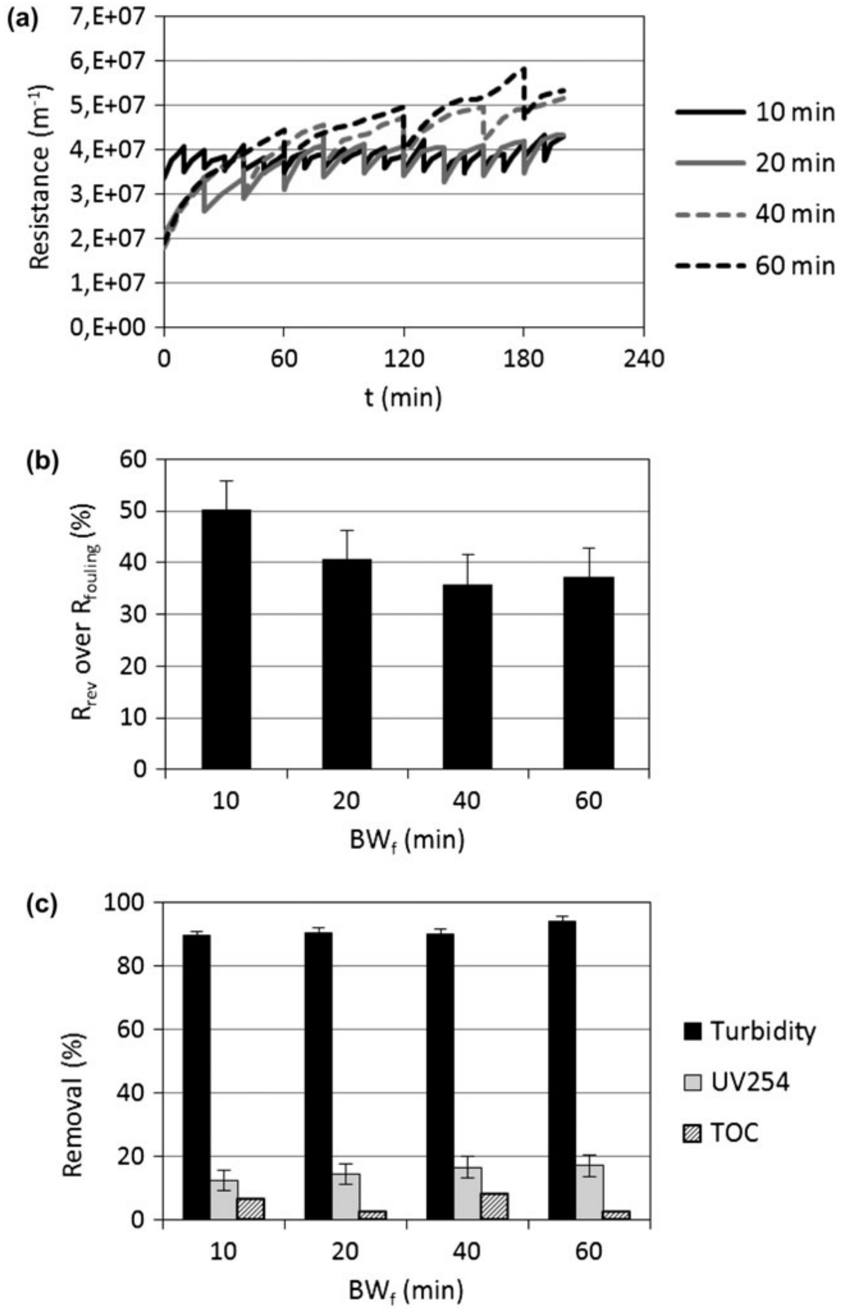

Fig. 4. Effect of BW_f on the (a) total resistance of the fouled membrane, (b) percentage of reversible fouling over the total membrane fouling, and (c) removal of turbidity, absorbance and TOC by the UF membrane. Error bars correspond to confidence intervals at a confidence level of 95% for all cases.

Increasing BW_d from 0.5 min to 1 min increased the fouling reversibility from 32 to 41%, indicating that foulants are more easily washed out away from the membrane pores during a longer backwash (Fig. 5(b)). In fact, better fouling removal from UF membrane at increased BW_d has been reported in the scientific literature for every variable filtration scenarios in terms of feed water characteristics and UF configurations [1,2,5,6,16–18], including other types of membrane systems such as MF [9], ceramic membranes [24] and membrane bioreactors [25].

In our study, lengthening the BW_d to 2 min was not accompanied by any increase in fouling reversibility. The existence of a threshold in BW_d beyond which

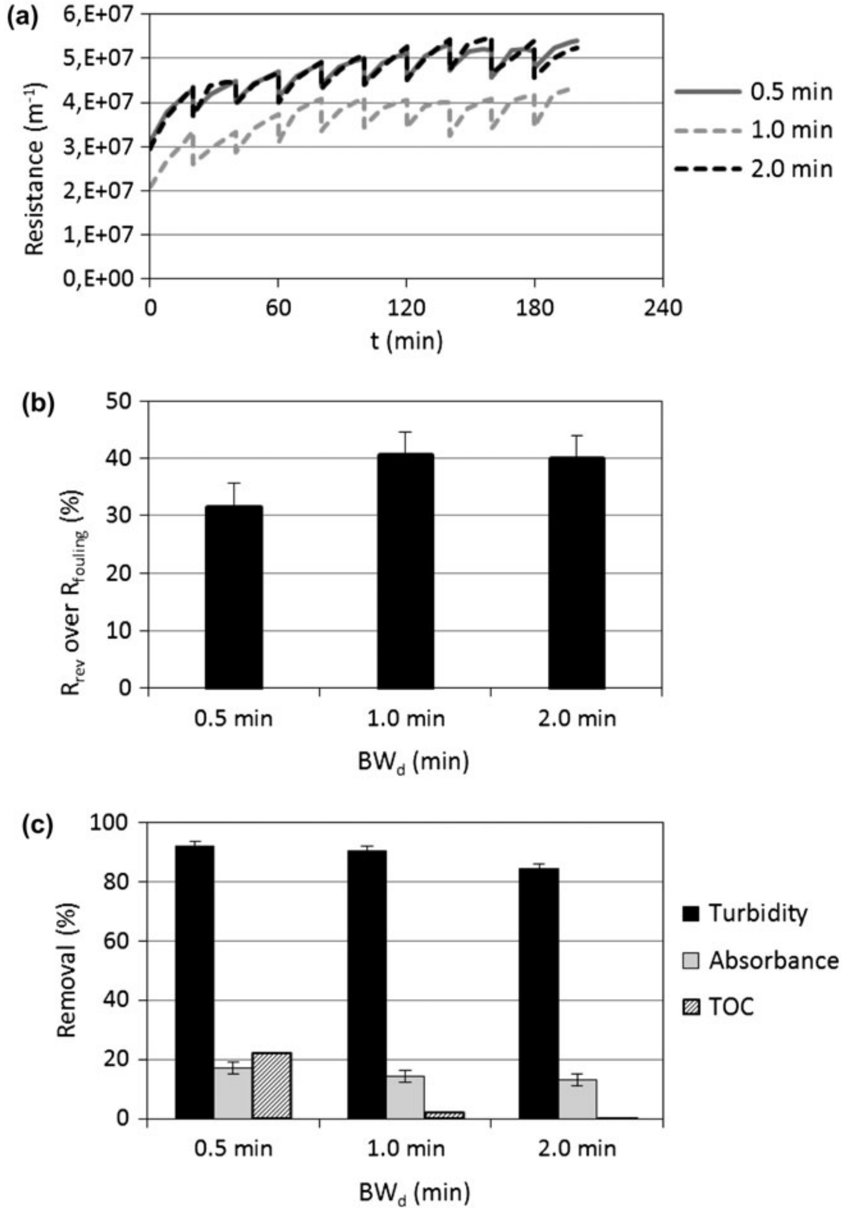

Fig. 5. Effect of BW_d on the (a) total resistance of the fouled membrane, (b) percentage of reversible fouling over the total membrane fouling, and (c) removal of turbidity, UV_{254} and TOC by the UF membrane. Error bars correspond to confidence intervals at a confidence level of 95% for cases.

no further improvement is observed has also been observed by other researchers [1,23]. Ye et al. [1] attributed this trend to the fact that "excess backwash volume might also foul the membrane or the remaining fouling cake due to the impurities in the backwash flux".

Similarly to the previous set of experiments, turbidity was removed at a high extent (89%), whereas UV_{254} and TOC removals averaged 15 and 9%, respectively (with the exception at BW_d of 0.5 when a TOC removal of 22% was attained).

3.4. *Effect of the chemically enhanced BW composition (BW_{CEB-c})*

The fouling rate and reversibility degree differed depending on the chemical cleaners used for the CEB (Fig. 6). NaClO performed the best, exhibiting the lowest fouling rate and the maximum fouling reversibility degree (approx. 38%), closely followed by the combination of NaOH + NaClO (approx. 34%). Acidic and alkaline cleaning solutions are commonly employed to remove inorganic and organic foulants, respectively, but the use of citric acid and NaOH in this study contributed little to the reversibility of fouling (approx. 28–27%) compared to the blank (UF permeate) (26%) (Fig. 6(b)).

These results compare well with those reported by other researchers, who found that NaClO as a cleaner added to the BW water performed the best at restoring the permeability of a UF membrane fouled after treatment of surface water [7] and wastewater [12,26], while NaOH had less influence compared to water. Similar results were observed by Espinasse et al. [27] after treating coupons of nanofiltration membrane with various cleaning agents. The benefits of using NaClO are explained by the fact that NaClO can oxidise the organic foulants accumulated on the membrane, generating more oxygen-containing functional groups (such as ketone, aldehyde and carboxylic acids), which due to their increased hydrophilicity are less attached to the membrane [12,28,29]. To exemplify the disinfection power of some chlorine-based compounds, Laine et al. [30] reported that ceasing the dosage of chlorine in backwash water after 20 d of operation resulted in severe fouling of the membranes within 5 d. Alkaline agents have also been reported to be effective at detaching foulants (particularly organic ones) since at high pH many organic compounds are hydrolysed presenting, under their dissociated form, increased solubility and propensity to be detached from the membrane [28].

Beyond the use of oxidant and alkaline agents separately, their combination has also been reported to be more effective at removing foulants from the membrane [28,29,31]. However, the combination of NaClO and NaOH in this study did not perform better than NaClO alone (Fig. 6). The low performance of citric acid, which is effective for the removal of inorganic foulants via dissolution of salts and complexation of certain metals, is indicative that the fouling layer formed on the membrane was made up of organic materials rather than inorganic salts.

3.5. Organic fouling composition on the UF membrane

Fig. 7 compares the concentration of TOC, DOC and each of the organic fraction in feed and permeate (with removal percentages in brackets) as analysed by HPSEC.

Feed water showed TOC and DOC values of 4.0 and 3.3 mg L^{-1}, respectively. This difference (of 15%)

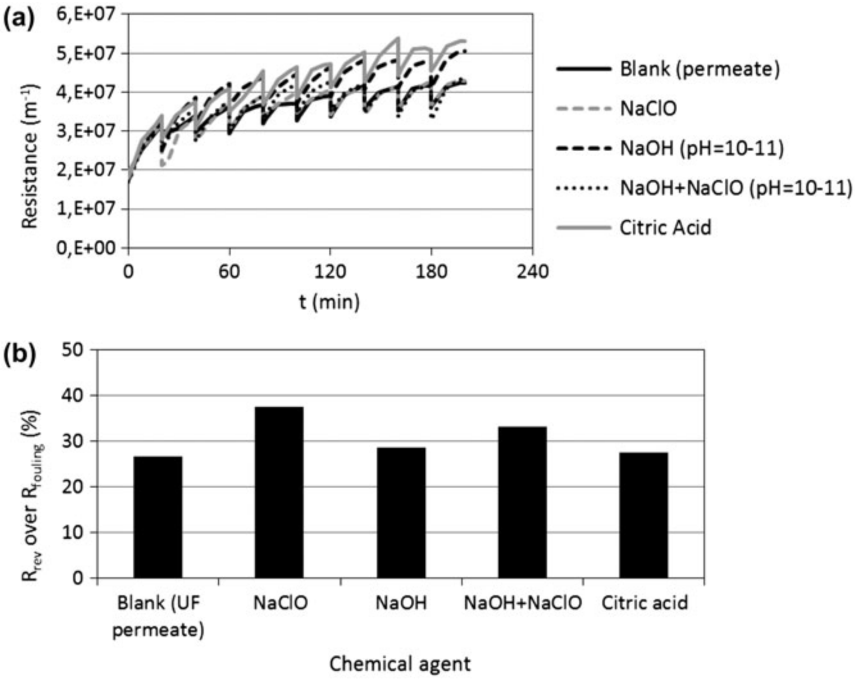

Fig. 6. Effect of the CEB composition ($BW_{CEB\text{-}c}$) on the (a) total resistance of the fouled membrane, (b) percentage of reversible fouling over the total membrane fouling by the UF membrane (confidence intervals ≤4.0% at a confidence level of 95% for all cases).

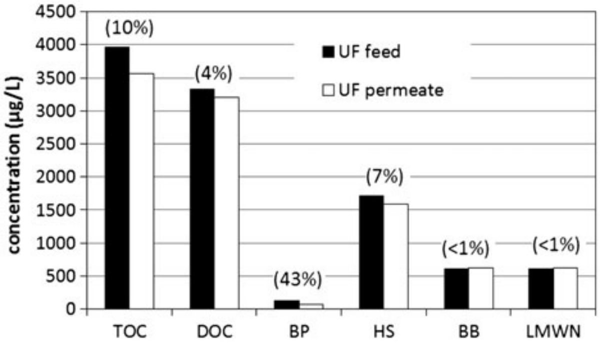

Fig. 7. Concentration of TOC, DOC and its fractions BP, HS, BB and LMWN in both feed and permeate streams (removal percentages by UF the membrane are in brackets).

indicated that after the coagulation/decantation stage, a fraction of the organic load was still in the form of particular or colloidal OC. With regard to the organic fractions, HS was always the most predominant one, accounting for 56% of the total DOC, followed by the lighter BB and LMWN (20%) fractions, while the heavier BP fraction averaged only 4%. The LMWA fraction was always found below limit detection. This composition is in accordance with previous studies that also applied HPSEC for the fractionation of DOC in drinking water plants [32,33].

The removal of TOC by the UF membrane was 10%, while the corresponding one for DOC was fairly low (4%). UF membrane preferentially removed the heaviest (and biggest) fraction BP (removal percentage of 43%), while intermediate HS was removed at a percentage of 7% and lighter (and smaller) BB and LMWN seemed to entirely pass through the UF membrane. This pattern is attributed to size-exclusion effects and is in accordance with published studies [22,34–37].

Based on a comparison between the composition of feed and permeate streams, fouling on UF membranes was anticipated to be made up of 67% HS (amounting 469 µg) and 33% BP (amounting 229 µg) (percentages referred to the total DOC removed by UF). It is of note that 20% of the 229 µg of BP retained on the UF membrane consisted of protein-like compounds, indicating preferential removal of polysaccharides over proteinaceous substances. This is in agreement with other researchers that have applied HPSEC in the UF of water [22].

3.6. Fouling detachment after BW and cleaning

UF membranes are periodically backwashed with ultrafiltered water to remove deposited matter from the membrane and restore its original permeability as much as possible. Detachment of organic matter from the UF membrane was evident as the backwash stream was richer in absolute TOC concentration (4.7 mg L^{-1}) than ultrafiltered water used for the backwash (3.6 mg L^{-1}). The composition of such backwash stream was 9% BP, 51% HS, 20% BB and 20% LMWN. In comparison with the ultrafiltered permeate, it was found to be enriched in BP (by 5%) and impoverished in HS (by 5%), while the concentrations of BB and LMWN were essentially the same.

Fig. 8 compares the initial organic mass (in µg) fouling and the UF membrane with the mass remaining after applying BW (+CEBs), CIP-B and CIP-A calculated through a mass balance from the concentration of each organic fraction within each volume stream.

It can be seen that BW (+CEBs) was able to detach 33% of the initial BP but only 9% of the initial HS. A similar pattern in the BP and HS detachment by BW is reported by Nguyen and Roddick in the UF of a municipal-activated sludge effluent [26]. The enrichment in BP suggested that components within this fraction, in particular polysaccharides rather than proteins, were not rigidly attached to the membrane but amenable to be washed out. This behaviour is likely due essentially to their size relative to that of the membrane pores: organic substances within the BP fraction much larger than the membrane pores lead to cake formation, which is more readily detached, while lighter fractions such as HS can cause pore blocking, build up a denser cake layer less readily washed out or be adsorbed onto the membrane material [8,26,30]. The remaining BP and HS on the membrane would

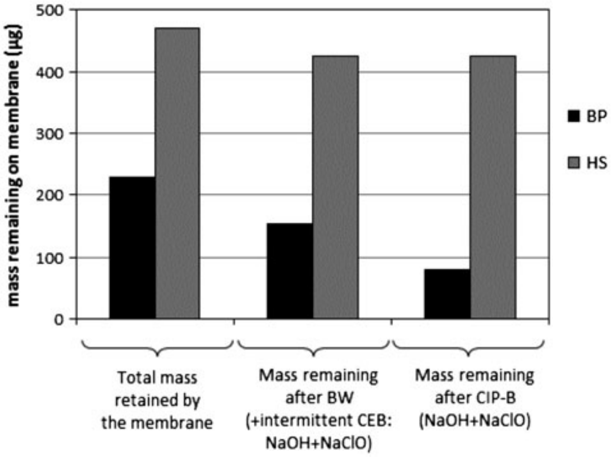

Fig. 8. Evolution of mass of BP and HS remaining on the UF membrane (µg) after the successive application of BW (+intermittent CEB: NaOH + NaClO) and CIP-B (NaOH + NaClO).

explain the irreversible fouling (never completely avoided whatever the BW regime applied) that resulted in the gradual increase in total resistance over time (Figs. 3–6). Which of these fractions has a larger impact on the membrane resistance is not clear.

HS was found in this study to be the most retained fraction in terms of amount (but not of percentage) (Fig. 7). HS is considered by some studies of minor relevance in terms of fouling due to their high transmission through the mesoporous UF membrane [22,34,37], whereas it is considered a detrimental foulant causing severe hydraulically irreversible fouling by some others [38,39].

Opposite to HS, BP was found to be the most retained fraction in terms of percentage (but not of amount) (Fig. 7), in agreement with other previous studies [20,22]. Its impact on fouling depends, however, upon its components: polysaccharides are believed to cause only hydraulically reversible fouling, while protein-like substances are thought to induce hydraulically irreversible fouling [22,37]. The major impact of proteins on fouling may be caused to the fact that they are more compact and can be retained at or inside the pores, thus resulting in the constriction and/or blockage of the membrane pores [37]. The finding in this study that 20% of the BP retained by the UF membrane was made of protein-like substances may explain why BP was not completely detached after the application of BW (+CEB) (Fig. 8).

In this study, because a portion of both BP and HS fractions was attached on the UF membrane, it could not be elucidated whether fouling was mainly caused by one or another (or both) fraction. Clearly, more investigations are required to identify if HS or BP contributes most to hydraulically (ir)reversible membrane fouling during UF of different waters.

Soaking the membrane with the CIP-B solution resulted in a detachment of a further 32% of the initial BP retained by the membrane, but on contrary no HS was detached at all, corroborating that this fraction was rigidly tight to the membrane and was not easily detached by NaOH neither by NaClO under the experimental conditions of this study. As mentioned above in this study, the detachment of BP may be explained by the fact that the constituents of the BP fraction (polysaccharides and proteins) are hydrolysed at high pH (even the weakest phenolic groups dissociate at such a high pH) and oxidised, increasing their solubility and therefore being more prone to be detached from the membrane [28]. Finally, the performance of an acid solution (CIP-A) 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 a cleaning agent. However, and also according with what was discussed in previous sections, organic fouling detachment is expected to be of minor importance since acid cleanings are applied commonly to eliminate inorganic foulants from the membrane (e.g. Fe and Mn) [31]. This is in qualitative agreement with Strugholtz et al., who found that NaOH and, in particular, NaClO were effective at removing both BP and HS while HCl was not [31]. The fact that organic fractions were analysed in their study only in the cleaning solution did not allow determine how much BP and HS were remaining on the membrane and, hence, compare results with the ones obtained in this study.

4. Discussion

Although differing in their efficiency, all BW regimes proved to contribute to control fouling on UF membranes. Nevertheless, results also showed that irreversible fouling was never completely avoided whatever the BW regime applied, resulting in a gradual increase in total resistance over time. Splitting the R_{fouling} into its components, it was found that R_{irrev} was always higher than R_{rev}.

The degree of reversibility depended on the BW-related variables. As expected, the more intensive the BW was (in terms of higher BW_{TMP}, shortened BW_{f} and prolonged BW_{d}) the more effective it was in removing foulants from the membrane. This was so because less intensive BW allowed more material to be accumulated on the membrane surface during filtration, forming a fouling layer more tightly attached and compacted and exhibiting thus a lower degree of reversibility under a given BW. Concerning the composition of CEB, NaClO performed the best and exhibiting the maximum fouling reversibility percentage (approx. 38%), closely followed by the combination of NaOH + NaClO (approx. 34%), while citric acid and NaOH contributed little (approx. 28–27%) compared to the blank (26%).

With regard to the permeate quality, no significant differences were observed whatever the BW regime applied. Turbidity removal was always above 88%, whereas Abs_{254} and TOC were decreased generally by 14–20 and 5–9%, respectively. The low retention of TOC may be explained by the predominance of small molecular weight (MW) organic fractions with MW ≤ 1,000 Da (much smaller than the nominal MWCO of the UF membrane of 300,000 Da) present in the decanted water.

From a produced water quality perspective, it appears clear, thus, that one of the main benefits of using UF was that, rather than removing TOC, it effectively reduced the load of suspended solids, colloidal matter and pathogens (responsible for the turbidity) that can foul and eventually block reverse osmosis membranes. This is noteworthy because current conventional pre-treatment methods of clarification and filtration are often ineffective at providing adequate turbidity or silt density index values required by RO membranes.

An issue that needs also to be bear in mind is that applying more intensive BW (in terms of higher BW_{TMP}, shortened BW_f, prolonged BW_d and dosage of a cleaning agent) results in reduced membrane fouling, but also leads to higher water losses, energy consumption and chemicals requirements, bringing down the operational efficiency of the UF treatment. A compromise solution must be taken to establish the optimal BW conditions that minimise both membrane fouling and total costs.

With regard to the fouling potential and reversibility of the organic fractions as analysed by HPSEC, UF membrane preferentially retained the heavier fraction BP (removal percentage of 43%), while intermediate HS was retained at a percentage of 7% and lighter (and smaller) BB and LMWN seemed to entirely pass through the UF membrane. This pattern was expected from size-exclusion effects [22,35,36]. Based on a mass balance over the UF membrane, fouling was anticipated to be made up of 67% HS and 33% BP.

The application of BW(+CEBs) resulted in the detachment of 33% of the initial BP but only 9% of the initial HS. This revealed that HS was more rigidly attached to the membrane, whereas BP (in particular, polysaccharides rather than protein-like substances) was more amenable to be washed out. Which of the fractions (BP or HS) remaining on the membrane contributed most on the irreversible fouling could not be elucidated in this study, but recent studies have concluded that protein-like substances represent a detrimental foulant that induces severe hydraulically irreversible fouling. This agrees with the finding that 20% of the BP fouling the UF membrane in this study consisted of proteinaceous materials.

Soaking the membrane with an alkaline and oxidant solution (CIP-B) resulted in the detachment of a further 32% of the initial BP retained by the membrane, while any detachment of HS was not observed. The performance of an acid solution (CIP-A) could not be quantified in this study because the organic fractions detached, if any, might be in the HPSEC chromatograms overwhelmed by the very high concentration of citric acid employed as a cleaning agent. However, organic fouling detachment is expected to be of minor importance since acid cleanings are applied commonly to eliminate inorganic foulants from the membrane.

5. Conclusions

In the light of the results, the following conclusions can be drawn:

(1) Irreversible fouling was never completely avoided whatever the BW regime applied, resulting in a gradual increase in total resistance over time.

(2) The degree of reversibility depended on the BW-related variables: the more intensive the BW was (in terms of higher BW_{TMP}, shortened BW_f and prolonged BW_d) the more effective it was in removing foulants from the membrane. Among all cleaning agents evaluated, NaClO performed the best at enhancing fouling reversibility. Therefore, a compromise solution must be taken to establish the optimal BW conditions that minimise both membrane fouling and total costs.

(3) Under all BW conditions assessed, turbidity removal was above 88%, whereas Abs_{254} and TOC were decreased generally by 14–20 and 5–9%, respectively. The main benefit of using UF was that, rather than removing TOC, it effectively reduced turbidity, which can foul and eventually block reverse osmosis membranes.

(4) Among all organic fractions, UF membrane preferentially retained the heavier BP (removal percentage of 43%), while intermediate HS was retained at a percentage of 7% and lighter (and smaller) BB and LMWN seemed to entirely pass through the UF membrane.

(5) The application of BW (with intermittent CEBs) resulted in the detachment of 33 and 9% of the initial BP and HS, respectively. Further application of an alkaline and oxidant solution (CIP-B) resulted in the detachment of a further 32% of the initial BP retained by the membrane, while any detachment of HS was not observed.

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