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Evaluation of MF and UF as pretreatments prior to RO applied to reclaim municipal wastewater for freshwater substitution in a paper mill: A practical experience

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ABSTRACT

A pilot plant study has been carried out to compare the effectiveness of different low pressure membrane systems (microfiltration and ultrafiltration) as pretreatments for a reverse osmosis system producing high quality reclaimed water from the effluent of a municipal wastewater treatment plant receiving a high percentage of industrial wastewater. The reclaimed water will be used to substitute fresh water in a paper mill. Although the implemented systems showed several problems derived from the unstable quality of the feed water, they were solid enough to keep a constant permeate quality; i.e. percentages of salt rejection above 99%, efficiencies in the removal of microorganisms to lower values than 1 CFU/100 mL, and final COD results below the detection limit ($<5\ \text{mg L}^{-1}$). In short, the quality of the produced reclaimed water was good enough to be used substituting fresh water in a paper mill. An enhanced monitoring of the quality of the water feeding the municipal wastewater treatment plant and an improved corresponding management of the treatments performed in there may be one of the keys to the success of this type of reclamation initiatives. Achieving constant disinfection, an appropriate design of the plants, and a good performance of cleaning operations were very important factors to be considered in order to fight against fouling. Temperature and the soaking time of chemical membrane cleanings were particularly well-optimized for the success of the treatment. Chloramines were compared to free chlorine as disinfection agent achieving satisfactory results.

1. Introduction

Spanish paper industry is one of the European leaders in paper recycling, using recovered paper as raw material at a rate higher than 84% [1], which particularly reaches the 100% in the Region of Madrid. The paper sector development (12% of the total National production) and the water scarcity in this region justify the need to develop and implement new sustainable processes that, besides being competitive and satisfying the demands of the society, introduce new environmentally friendlier technologies.

In the paper industry, water is mainly used as process, cleaning, cooling and boiler-feed water. Paper is formed from a diluted suspension ($10\ \text{g L}^{-1}$) of cellulose fibres, mineral fillers and additives. From the point of view of paper quality, the water introduced in the paper machine (mainly in the forming wire showers) must meet high quality requirements, as the wires must be continuously kept well cleaned to achieve both an optimum paper sheet and drainage. On the other hand, chemicals are also prepared with fresh water, as its efficiency may be affected by the quality of preparation water [2,3].

Although water is recycled within the mill at a high level, a total closure of the water circuit is not recommended for graphic papers as there are some technical limitations due to the accumulation of contaminants inside the circuits (salts, dissolved and organic matter, micro-contaminants and microorganisms), which affect the production process and the paper quality [4,5].

The use of reclaimed water has been already reported some decades ago and nowadays it represents a promising expanding market [6]. However, most of this reclaimed water is still used in agricultural and urban applications [6]. In fact, only a low percentage of the total reclaimed water is nowadays used for industrial purposes, where it is mainly (>50%) used as cooling water [7]. On the other hand, it is also true that the quantity of industrial effluents dumped to municipal wastewater treatment plants (mWWTP) is usually low, which is not the case.

Particularly, paper mills are devoting a great effort to reduce freshwater consumption recycling their own effluents for different purposes. For example, membrane technology (UF mainly) is being

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Table 1
Water quality requirements for HPM freshwater, Spanish drinking water, NEWater target quality, and USEPA/WHO standards for drinking water.

Parameter	Units	HPM[a]	Spanish regulation[b]	NEWater[c]	USEPA/WHO[d]
pH		6.5–7.5	6.5–9.5	7.0–8.5	6.5–8.5/–[e]
Conductivity	$\mu S\,cm^{-1}$	<500	2500	<200	(–/–)[e]
TSS	$mg\,L^{-1}$	<5	–[e]	–[e]	(–/–)[e]
Total COD	$mg\,L^{-1}$	<5	–[e]	–[e]	(–/–)[e]
Sulphates	$mg\,L^{-1}$	<200	250	<5	250/250
Dissolved silica (SiO_2)	$mgSi\,L^{-1}$	<5	–[e]	<3	(–/–)[e]
Chlorides	$mg\,L^{-1}$	<50	250	<20	250/250
Hardness	$mgCaCO_3\,L^{-1}$	<200	–[e]	<20	[f]
Calcium	$mgCa\,L^{-1}$	<60	–[e]	4–20	(–/–)[e]
Magnesium	$mg\,L^{-1}$	<15	–[e]	–[e]	(–/–)[e]
Alkalinity	$mgCaCO_3\,L^{-1}$	<100	–[e]	–[e]	(–/–)[e]
Iron	$mg\,L^{-1}$	<0.1	0.2	<0.04	0.3/0.3
Aluminium	$mg\,L^{-1}$	<0.1	0.2	<0.1	0.05–0.2/0.2
Manganese	$mg\,L^{-1}$	<0.05	0.05	<0.05	0.05/0.4
Ammoniacal-nitrogen	$mgN\,L^{-1}$	<0.5	0.5	<1.0	–[e]/1.2
Nitrates	$mgNO_3\,L^{-1}$	<1	50	<15	10/11
Phosphorous	$mgP\,L^{-1}$	<0.2	–[e]	–[e]	(–/–)[e]

[a] HPM (personal communication).
[b] Spanish Royal Decree, RD 140/2003.
[c] Public Utilities Board of Singapore (2003).
[d] US Environmental Protection Agency (1996) and Water Health Organization (1998).
[e] Non-specified.
[f] Non-available.

used for the recirculation of process water in some paper mills [8,9]. As a result, *Stora Enso Uetersen's PM1* (Croatia) has dropped its fresh water consumption by 15–20% [8], and *Arctic Paper Munkedals mill* (Sweden) has reduced the fresh water use to less than 3 $m^3\,t^{-1}$ of paper in 2003 [10,11].

In addition, some paper mills are working in the use of multi-barrier membrane treatments for reclaiming their own effluents. For example, Mänttäri et al. [12] compared different UF, NF, and RO membranes to treat part of the effluent of the *Stora Enso Kotka mill* (Finland), but the RO permeability was as low as 2.5 $L\,m^{-2}\,h^{-1}\,bar^{-1}$. *McKinley Paper Mill* (New Mexico, USA), which produces linerboard from 100% recycled board and old corrugated containers, uses a MF + RO system to recycle all the effluent within the mill. This paper mill is nowadays consuming only 1.2 m^3 of freshwater per tonne of produced paper. This water consumption is mainly produced by evaporation during paperboard drying [13].

Finally, the combination of NF and electrodialysis has been proposed as the best alternative to remove organochlorinated compounds and salts from the stream obtained from alkaline bleaching in kraft pulp mills [14–17]; and the application of UF and NF membranes to treat both, paper mill clear filtrated waters and effluents, has been recommended [18–20].

Although several paper mills have reported their effort in reducing fresh water use by applying membrane technologies within the process, and by recycling their own effluent, freshwater substitution by municipal reclaimed water has also been addressed in three paper mills (Mondi Paper Mill, Durban, South Africa; SCA Tissue Flagstaff Mill, Arizona, USA; and Blue Heron Paper, Georgia, USA). The mWWTPs that supply reclaimed water to these paper mills are not using membrane technologies in any case [21,22].

HOLMEN Paper Madrid (HPM) in Spain produces 470,000 $t\,y^{-1}$ of newsprint and coated paper from 100% recovered paper. As a consequence of its location, this paper mill consumes fresh water coming directly from the regional drinkable-water facilities, managed by the regional-owned company "*Canal de Isabel II*". After optimizing the water circuits and implementing internal water treatments, the fresh water consumption in the mill is currently lower than 8 $m^3\,t^{-1}$ of paper produced, which is the lowest water consumption in Europe for these products. In fact, this level is below the quantity stated by the corresponding European BREF (reference document on best available techniques) for the Pulp and Paper Industry (<10 $m^3\,t^{-1}$, for recycled newsprint production) [23]. However, the current net water consumption value is still high if we consider that it represents the 17.3% of the total industrial water used in the Region of Madrid.

The greatest fresh water consumption inside the mill is hold by the high pressure showers of the paper machine, which are needed to clean the wires of paper formation and press section in continuous. The minimum water quality requirements that must be met in this process in order to avoid scaling, corrosion [24], biofouling, losses in retention aid efficiencies, and runnability problems in the paper machine [5] are shown in Table 1. Furthermore, water quality criteria must also consider health risks derived from the spread out of process water as aerosols that may reach workers. Therefore, the removal of pathogens (bacteria, helminths, protozoa and enteric viruses) must be primarily achieved by the applied reclamation processes [25], and a posterior disinfection step by ultraviolet (UV) radiation [26].

This paper presents the results of a pilot study carried out to evaluate the feasibility of these multi-barrier membrane systems to produce reclaimed water from a mWWTP (receiving a high percentage of industrial effluent) for its use as process water in a paper mill.

2. Materials and methods

2.1. Pilot plants configuration

The pilot trials were run in a municipal wastewater treatment plant (mWWTP) located in the Region of Madrid (Spain). This plant has a designed capacity of 129,600 $m^3\,d^{-1}$, which is the equivalent to a population of 1,225,000 inhabitants. This mWWTP does not only treat municipal wastewater, but also an important amount of industrial effluents.

As it is shown in Fig. 1, the pilot study compares three multi-barrier membrane systems based on the following layout: MF/UF + RO + UV. RO filtration and UV disinfection were the same in all the lines. Three different MF or UF units were implemented, as shown in Table 2, to select the best pretreatment for the RO unit. The water intake to the membrane systems was taken from a storage tank containing tertiary treated water, which treatment consisted in coagulation-flocculation based on $FeCl_3$ and polyacrylamide addition, a sand filtration and a final disinfection with sodium hypochlorite (NaClO).

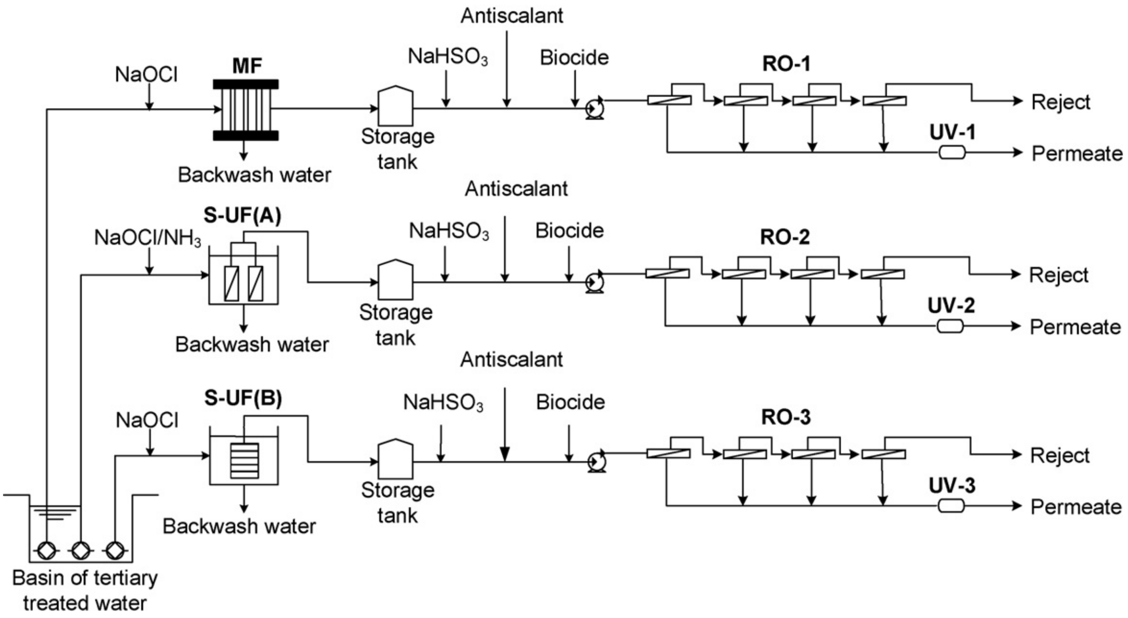

Fig. 1. Configuration of the pilot plants implemented for comparing the designed three alternative membrane treatments to reclaim wastewater.

2.1.1. *Chemical disinfection*

A certain disinfection grade was ensured in all the lines to avoid the impact of biofouling in the MF/UF membranes, and biogrowth in dead zones and storage tanks. Moreover, although MF and UF membranes are able to remove high levels of bacteria, protozoan cysts and oocysts; it has been reported that only one-third to greater than 6-logs removals of viruses are achieved, thus remaining in the permeate and reaching RO membranes [27,28]. As free chlorine content was not constant in the tertiary water, chlorine was externally dosed as NaClO (1 mg L^{-1}) before the pretreatments. In this way, a concentration of free chlorine between 0.5 and 1.0 mg L^{-1} was always ensured in the lines [29].

This disinfection system was compared to the addition of chloramines. Although the reaction mechanism of chloramines is slower, their retention time in the pipes is longer, and they have less tendency to react with the organics present in water. Therefore, lower amounts of disinfection by-products (DBP's) are formed [29,30]. As chloramines are weaker oxidants than aqueous chlorine, they are compatible with polyamide membranes in some applications [31]. Typically, low fouling composite (LFC) and polyamide membranes show a tolerance to chloramines of 150,000 to 300,000 mg L^{-1} h^{-1} before detecting noticeable increases in salt passages [32].

The addition of chloramines started when RO membranes from supplier B were installed, since they were not compatible with RO membranes from supplier A (RO operation conditions are shown in Table 3). 2 mg L^{-1} NH$_3$ and 3 mg L^{-1} NaClO were added before in-flowing to the S-UF$_A$ unit to ensure a 2 mg L^{-1} make-up of chloramines in the whole line [33].

Table 2
Specifications of the tested MF and UF membranes.

	Units	MF	UF(A)	UF(B)
System	–	Pressurized	Submerged	Submerged
Membrane	–	Hollow fibre	Spiral wound	Hollow fibre
Material	–	PVDF	PES	PVDF
Nominal pore size	μm	0.05	0.05	0.02
Total membrane area	m^2	46.8	66.0	139.5
Flux direction	–	Outside-in	Outside-in	Outside-in
Maximum TMP	bar	1.30	−0.70	−0.70

TMP = Transmembrane pressure; PVDF = polyvinylidene fluoride; PES = polyethersulfone.

In addition to chemical disinfection, 150 mg L^{-1} of biocide was added for 1 h weekly to all the lines. When chloramines were used, the biocide was not dosed in the S-UF$_A$ line. The objective of biocide addition is substituting the effect of chlorine after it is eliminated by NaHSO$_3$ addition. As the passage of chloramines into the permeate is relatively high, and it reaches up to the 80% of the feed level, there is no need for additional biocide dosing [32].

2.1.2. *Microfiltration unit*

The water that fed this module passed before through a 3 mm security filter. The system worked in dead-end mode with an outside-in-type filtration made up of hollow fibre membranes.

After a defined filtration time, a 2.5 min backwash was performed. First of all, the external surface of the fibres is aerated to promote the removal of the deposited matter on them. Afterwards, the permeate water, already inside the fibres, is forced to pass from the inlet to the outlet of the fibres; and then, all the cleaning water contained inside the membrane module is drained as a reject stream. Finally, a permeate flow was injected to flush all the remaining matter inside the unit. After all, the MF unit produced 0.33 m^3 of concentrate per backwash.

A two-phase chemical cleaning-in-place (CIP) of the MF module was programmed weekly. An acid cleaning stage was performed first mixing citric acid at a concentration of 1.9% with phosphoric acid at a concentration of 0.1–0.2%, reaching pH 2. Temperature was kept at 35 °C. Then, NaClO at a free chlorine concentration of 0.04% was added at a temperature of 25 °C. In both phases, clean-

Table 3
Operating conditions for the reverse osmosis membranes.

	Units	Supplier A	Supplier B
Material	–	Polyamide	Polyamide
Specific surface	m^2	7.6	7.9
Permeate flow	L h^{-1}	530	520
Reject flow	L h^{-1}	1000	1000
Recovery	%	34.6	34.2
Maximum pressure work	bar	41	41
Maximum temperature work	°C	45	45
pH working range	–	2–11	3–10
Maximum SDI$_{15}$	–	5	5
Maximum free chlorine allowed	mg L^{-1}	<0.1	<0.1

SDI$_{15}$ = 15-min silt density index.

ing solutions were recirculated without filtration for 30 min; and a soaking step was performed for 30 min. Another recirculation was then run for 20 min, and the chemical solution was finally drained down. Filtration with fresh water and a final backwash were always performed before starting normal filtration. As the membranes are subjected to mechanical stress during filtration and backwash periods, fibres may be damaged, so pressure decay tests (PDT) were run weekly following the ASTM D6908-06 standard [34].

2.1.3. Submerged ultrafiltration unit with spiral wound membranes (S-UF$_A$)

Tertiary treated water was first filtered through a 500 μm filter. S-UF$_A$ consisted of four spiral wound membranes immersed into the feeding tank and a centrifugal pump, which creates a vacuum from the top of the modules, withdrawing permeate from the membranes at a maximum vacuum pressure of −0.7 bar. This permeate was collected in a tank and reused for the periodical backwashes. At the end of every backwash, the membrane tank was emptied, so the interval between backwashes must be appropriately selected in order to keep a high recovery rate, which value was optimized along the performance of the trial. As a result, the membrane tank dumped 0.292 m^3 of water (0.073 m^3 per membrane element) in each drainage stage. During filtration, air was bubbled up through the bottom of the elements to remove fouling matter via air scouring.

Membranes were also chemically cleaned. The duration of each step, the type of chemicals used and their concentration were optimized along the trial.

2.1.4. Submerged ultrafiltration unit with hollow fibre membranes (S-UF$_B$)

Feed water was previously filtered through a 500 μm filter. Hollow fibres were located horizontally and wastewater was filtered by applying vacuum (0.7 bar) at the end of each fibre module. Rejected particles remained in the process tank and were periodically removed by backwashes with permeated water. Simultaneously, aeration scours any solid attached on the surface of the fibres.

Chemical cleanings were carried out by draining the membrane tank and soaking the fibres inside a cleaning solution for several minutes. After the solution was drained, chemical residues were flushed from the membranes before the system returned to normal operation. As described for S-UF$_A$, the duration of each step, the type of chemicals used and their concentrations were optimized along the trial.

2.1.5. Reverse osmosis (RO)

The three RO plants were configured in one pass and four stages, and they started running with spiral wound membranes from the same supplier (A). After 2 months operating, RO-2 membranes were changed for similar ones from a different supplier (B). RO operation conditions are shown in Table 3. There are non-significant differences in their main characteristics.

Before entering RO membranes, feed water passes through a 5 μm cartridge filter forced by a low pressure pump (3.5–4.0 bar), then 4 mg L^{-1} anti-scalant (PermaTreat®PC-191, Nalco Company, Naperville, IL, USA) and 8 mg L^{-1} sodium bisulphite ($NaHSO_3$) were dosed to remove any trace of free chlorine to avoid the oxidation of the polyamide [35,36].

Silt density index after 15 min (SDI$_{15}$) was determined daily, following the ASTM D4189-07 standard [37] and using a SDI-2000 equipment (Millipore, Billerica, MA, USA), to test the fouling potential of the water.

Different combinations of products, temperatures, and washing and soaking times, were performed to find the most effective cleaning procedure. All PermaClean® and Ultrasil10® products were supplied by Nalco Company (Naperville, IL, USA).

Finally, the permeate from RO plants was ultimately treated in a 27 W UV unit (TrojanUVMax^{TM}, London, Ontario, Canada) to ensure its final disinfection [38].

2.2. Analyses

Water samples were taken from the inlet, permeate and reject fractions of each implemented membrane system. Temperature, pH, conductivity, turbidity and free chlorine were measured daily. Chemical oxygen demand (COD), 5-days biological oxygen demand (BOD$_5$), total suspended solids (TSS), nitrogen compounds, phosphorous species, iron, aluminium and silica contents were analyzed twice a week. All water analyses were carried out according to the *Standard Methods for Examination of Water and Wastewater* (2005) [39]. Furthermore, autopsies of all MF, UF and RO membranes were done at the end of the trials. The following analytical techniques were used to determine the nature of the membrane foulants present on their surface:

- Fourier Transform Infrared spectroscopy (FRA106/S FTIR spectrophotometer, Bruker Optics, USA) was used to determine the nature of organic foulants [40].
- Scanning Electron Microscopy (SEM) was applied to see the structure of both, foulants and membrane layer [41]. A JSM-5610 Scanning Electron Microscope (JEOL, Japan) was used to perform these analyses.
- Energy dispersive X-ray (EDX) was used to identify inorganic foulants [41]. X-ray micro-analyses were carried out assisting SEM measurements with an Energy dispersive X-ray spectrometer (ISIS, Oxford Instruments, UK).
- As RO membranes were made of polyamide, Fujiwara tests were conducted to assess membrane exposure to halogenated organics such as chlorine, which is probably the most valid current indicator. Small pieces of membrane were put into a solution of 10 mL of NaOH 10 M and 10 mL of pyridine. This solution was afterwards placed in a boiling water bath for 2 min. If the solution turns red or pink colour, it means that the membrane has been oxidized by chlorine, or other halogen [42].
- Dye tests were performed to determine if membranes suffered oxidative damage [34]. These tests consist of dropping a small quantity of a dying solution on the membrane surface. The dye will then readily adhere to the support material if there are damaged areas in the membrane barrier layer. These damaged areas turn into bright pink spots when they are exposed to the dye.
- The loss on ignition (LOI) method was applied to S-UF$_A$ membranes to determine the organic weight fraction of the foulant, which is first dried at 110 °C, and then burnt at 950 °C [43].

2.3. Operational variables

Temperature, pH, turbidity, flow rates and applied pressures were recorded in a data-logger installed in each pilot plant. Furthermore, transmembrane pressure (TMP) and permeability were determined. As flow rates were fixed by design decision, increases in TMP are the result of membrane fouling. Permeability results after dividing the membrane-area-normalized flux by the TMP considering an exponential temperature correction factor. As water gets colder, its viscosity increases, making the passage through the membrane pores more difficult; hence reducing its permeability. Equation 1 was used to calculate the permeability (L) of MF and UF systems [44].

$$L_{20} = \left(\frac{J}{\Delta P}\right) \cdot \exp(-0.032 \cdot (20 - T)) \qquad (1)$$

where L_{20} is the membrane permeability at 20 °C (L m^{-2} bar^{-1} h^{-1}); J is the permeate flux (L h^{-1} m^{-2}); ΔP is the transmembrane pressure (bar); and T is the temperature of water (°C).

Table 4
Schedule followed to test the MF and submerged UF pretreatments to the reverse osmosis.

Stage	Flux (L m^{-2} h^{-1})			Time between backwashes (min)		
	MF	S-UF$_A$	S-UF$_B$	MF	S-UF$_A$	S-UF$_B$
I	36.0	30.0	34.0	22.0	15.0	30.0
II	43.0	34.0	43.0	22.0	15.0	30.0
III	49.0	26.0	38.0	22.0	15.0	25.0
IV	36.0	28.0	28.0	18.0	15.0	20.0
V[a]	41.0	29.0	27.0	20.0	65.0	23.5
VI[b]	45.0	33.4	36.0	18.0	59.0	15.0

[a] Demonstration stage under optimal conditions.
[b] $N-1$ conditions.

A feed temperature drop of 4 °C causes a permeate flow decrease of about a 10% in RO systems. Therefore, to evaluate changes in the performance of these systems over time, and compare their behaviour, all fluxes were normalized to a reference temperature. 25 °C was chosen for RO membranes and 20 °C was set for MF and UF pretreatments [44]. Considering the above, when the normalized flux decreased, or the differential pressure increased, a 10–15%, a chemical cleaning was run to recover the initial performance of the membranes [45].

2.4. Schedule

This pilot study lasted 4 months, and it was divided in six stages (I–VI), where different fluxes and time gaps between backwashes in the MF and UF membrane systems were tested, as shown in Table 4. The schedule was set to start in a conservative flux, and then, increase and modulate its value until finding the maximum flux value at which the membrane can work without a continuous TMP increase that make backwashes to be ineffective. The selection of the time gap between backwashes was set in order to find a balance between a high recovery rate and a low chemical cleaning frequency. The recovery rate (R) was calculated according to the following equation:

$$R = 100 \cdot \left(1 - \frac{Q_{bw}}{Q}\right) \qquad (2)$$

where R is the recovery rate (%); Q_{bw} is the backwash flow rate (L h^{-1}); and Q is the feed-water flow rate (L h^{-1}).

Stage V of the study combined the optimal values of flux and time between backwashes tested in previous stages, thus representing a real demonstration stage of the trial; and in stage VI, the plant was forced to run 24 h under higher production conditions, simulating the performance of the full plant while one of the membrane frames is stopped for maintenance or cleaning operations, which is commonly known as N-1 condition.

3. Results and discussion

3.1. Quality of the tertiary treated water

Water quality fed to the pilot plants did not remain stable along the trial, as revealed by the maximum-minimum range of values monitored in the tertiary treated water (Table 5). The temperature of the water varied from 11 to 21 °C depending on the weather conditions; and pH remained between 6.5 and 7.5 during all the trial. This pH decrease was probably caused by the higher dosing of $FeCl_3$ performed in the secondary treatment to favour phosphorous removal.

Conductivity remained below 1.2 mS cm^{-1} until the end of November, and then increased up to 1.5 mS cm^{-1}. As the tertiary treated water fed to the MF or UF systems was stored in a basin, hard autumn rains during the experimental period had a diluting effect; thus lowering conductivity. It was also remarkable that, during Christmas holidays, an important number of industries that dump into this mWWTP performed chemical cleanings in their lines, thus increasing the contamination load of the wastewater. Conductivity increased in particular.

Turbidity was always kept below 10 NTU; and total nitrogen and total phosphorous remained below 30 and 5 mg L^{-1}, respectively. Calcium content showed a steady behaviour as well, remaining always between 31 and 47 mg L^{-1} (Table 5). While COD was always kept below 60 mg L^{-1} along the whole experimental period, BOD_5 and TSS did not exceeded 11 and 15 mg L^{-1}, respectively. Maximum values were registered after Christmas holidays (Fig. 2).

Silica, iron and aluminium contents were also monitored along the trial as they may produce scaling. Regarding silica, it is present in water as monosilicic acid (H_4SiO_4), a weak acid that is generally deionized at neutral pH. As pH was always kept under 7.5, hydrolyzation did not represent an important problem in the performance of the trials although the silica content increased significantly from December thereafter (Fig. 2). While aluminium content was always below 0.6 mg L^{-1}, iron concentrations began to increase over 0.5 mg L^{-1} from mid-December onwards as well (Fig. 2), being susceptible to form insoluble precipitates of $Fe(OH)_3$ [46,47], as it was specially observed in S-UF$_B$.

Finally, to avoid the formation of magnesium silicates at pH <7.5, silica (as SiO_2) must be kept below 200 mg L^{-1}, and the product between Mg (expressed as $CaCO_3$) and Si (as SiO_2) contents must be less than 40,000 [48]. Both requisites were accomplished along

Table 5
Maximum and minimum values for the quality of the feed water and MF/UF permeates.

Parameter	Units	Tertiary water[a]	MF out	UF(A) out	UF(B) out
pH		6.5–7.5	6.6–7.3	7.1–7.9	6.6–7.4
Conductivity	μS cm^{-1}	910–1500	912–1359	912–1328	918–1336
TSS	mg L^{-1}	2.0–15.0	<2	<2	<2
Total COD	mg L^{-1}	23–58	8–45	21–47	27–45
BOD_5	mg L^{-1}	5–11	1–8	1–8	2–8
Sulphates	mg L^{-1}	123–314	130–302	119–296	116–286
Dissolved silica (as SiO_2)	mg L^{-1}	1.9–20.0	1.2–20	3.9–18	4.0–20
Chlorides	mg L^{-1}	74–176	81–178	87–179	76–175
Hardness	mgCaCO$_3$ L^{-1}	120–147	120–147	120–144	123–147
Calcium	mgCa L^{-1}	31–47	31–44	32–40	31–40
Magnesium	mg L^{-1}	6–13	6–12	7–12	6–12
Bicarbonates	mg L^{-1}	148–260	74–239	79–236	77–241
Iron	mg L^{-1}	0.016–3.800	0.038–0.170	0.027–0.090	0.028–0.130
Aluminium	mg L^{-1}	0.068–0.590	0.038–0.480	0.036–0.070	0.066–0.470
Manganese	mg L^{-1}	0.06–0.10	0.06–0.21	0.06–0.21	0.06–0.19

[a] The municipal WWTP was under a starting-up period.

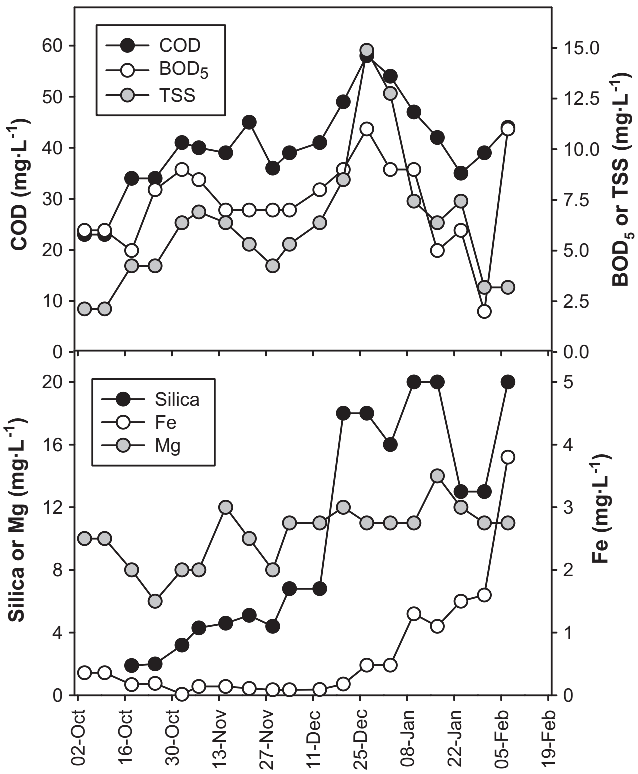

Fig. 2. Evolution of silica, iron, magnesium, COD and BOD_5 contents in the tertiary treated water used to feed the treatment plants.

the trials, as Mg and silica contents were always kept below 13 and 20 mg L^{-1}, respectively (Table 5).

3.2. Performance of the MF plant

Fig. 3 shows the performance of the MF system along the trial. As flux was increased in the three first stages of the experiment, TMP also increased, while permeability showed a decreasing tendency. Backwashes and chemical cleanings performed weekly kept the system stable. The performance of the membranes resulted worse during stage III, from December 5th, when COD, TSS and silica content began to rise in the feed water, and a long weekend started (Fig. 2). As result, TMP strongly increased, but it turned down again after a chemical cleaning for a very short time. Fortunately, none of the membranes needed to be changed, and none of the security filters suffered blockage after this fouling incident.

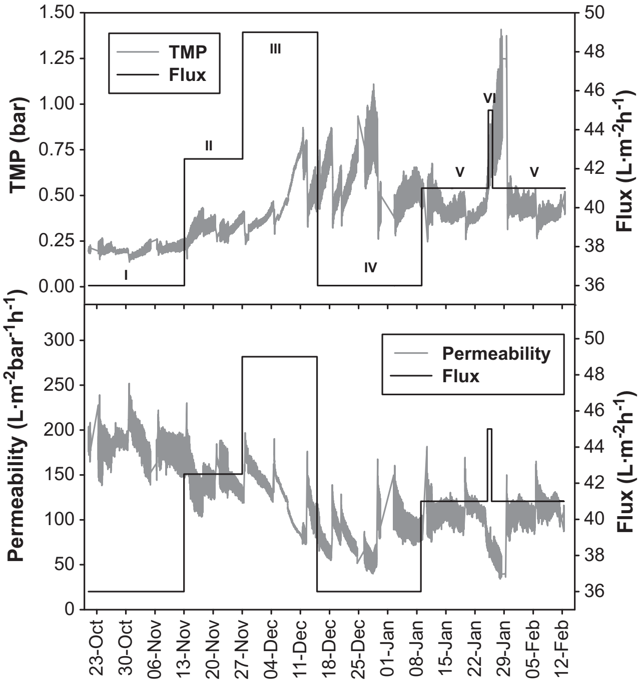

Fig. 3. Evolution of permeability and transmembrane pressure (TMP) across every stage (I–VI) of the pilot trials in the MF system.

As feed water quality turned worse, and TMP increased quickly despite the performed chemical cleaning, operating flux was reduced in stage IV to the same value of stage I, trying to recover stability in the system. However, TMP kept increasing until December 30th, when the pilot plants were stopped for New Year's long weekend, as well as the tertiary treatment of the mWWTP. This unsteady performance was attributed to maintenance and cleaning operations performed in the mills that dump effluents to this mWWTP, taking advantage of production stop during holidays. During this time, both oil and grease were found in the tertiary water at a concentration of 2 mg L^{-1}. Therefore, an appropriate management of the previous tertiary treatment is recommended to avoid an excessive damage to the membranes during these periods of time, especially in mWWTP fed with a high load of industrial wastewaters that show a great variability of characteristics due to production schedules.

The plant was re-started up on January 2nd under stage IV operational conditions, trying to reach certain working stability before progressing to the next stage. Along stage V, the system ran approximately 1 month at the best operational conditions selected from the previous information: $J = 41\,L\,m^{-2}\,h^{-1}$, 20 min between backwashes, and weekly CIP operations.

During this demonstration stage (V), another change in water quality happened, and TMP reached 1.3 bar, the maximum allowed pressure for this type of membrane. Although iron concentration in the feed water began to increase from mid-December onwards, it was not until the January 22nd, matching up with this TMP increase, when its value raised over 1.5 mg L^{-1} (Fig. 2), severely affecting the system. This fouling episode did not affect the membranes irreversibly, and they recovered TMP optimal values as soon as chemical cleaning was performed. As backwashes were run every 20 min, hardly scouring the membranes with air, the foulant cake did not have enough time to get embedded into the membrane.

Within the demonstration stage, one day was assigned to perform the stage VI trial ($J = 45\,L\,m^{-2}\,h^{-1}$ and 18 min between backwashes). As the system was working forcing more the operational conditions, backwashes were run more frequently. In this way, the unit was capable of recovering the initial conditions of TMP and permeability. Although the quick increase of TMP could be attributed to these forced operation regime in first instance, the S-UF_A system also experienced high TMP values without operating at those conditions.

Finally, membrane fibres were analyzed by SEM-EDX after the trials in order to analyze the fouling of the membranes. The fouling layer was composed by: C (54.1%), Si (26.1%), F (10.4%), O (8.4%), Cu (0.5%), Cl (0.3%), Na (0.1%), Ca (0.1%) and Zn (0.1%).

3.3. Performance of the S-UF_A plant

Along the first two stages of performance (I–II), this unit started working without draining the tank of membranes after backwashing in order to keep the recovery rate as high as possible, as backwashes were run every 15 min. These conditions of operation produced an irreversible fouling due to the accumulation of foulants and the growth of microorganisms, which drove the system to reach the maximum allowable TMP (−0.70 bar) in a few weeks (Fig. 4), with the consequence of disc rupture breakage. The

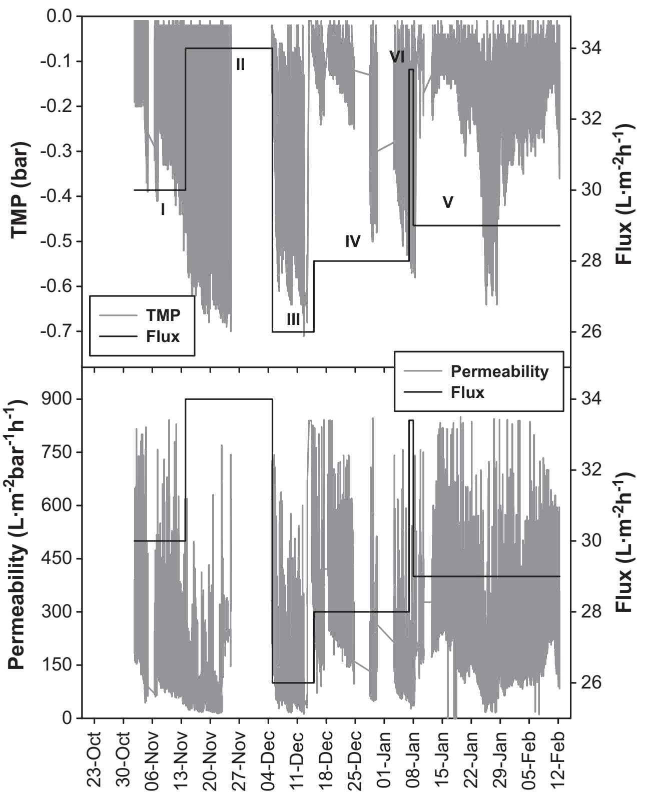

Fig. 4. Evolution of permeability and transmembrane pressure (TMP) across every stage (I–VI) of the pilot trials in the submerged UF system A (S-UF$_A$).

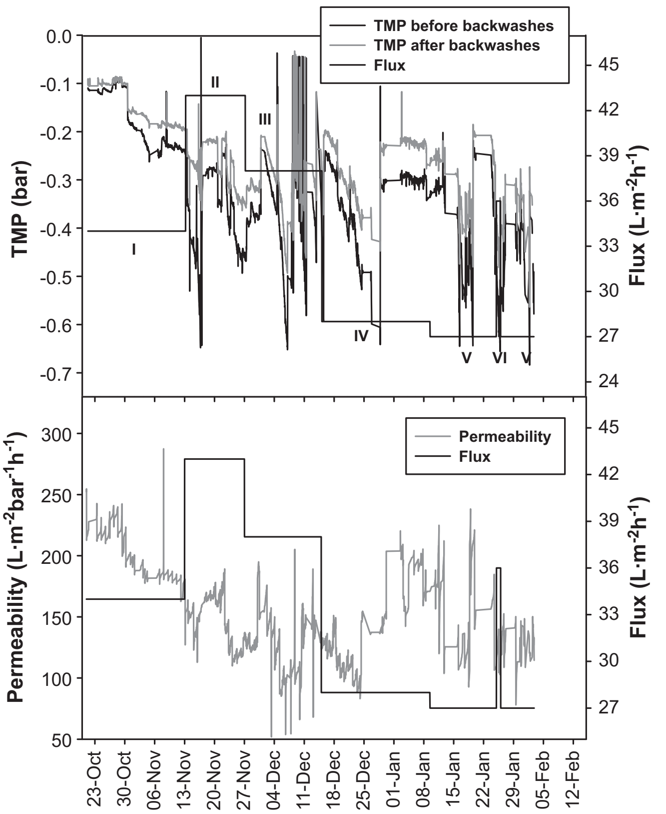

Fig. 5. Evolution of permeability and transmembrane pressure (TMP) across every stage (I–VI) of the pilot trials in the submerged UF system B (S-UF$_B$).

system kept stopped until December 5th, when the breakage disc was repaired.

Stage III started then, at a lower flux (26 L m^{-2} h^{-1}). Just at the beginning of this phase, one of the membrane modules left down into the membrane tank. Although it was fixed again as soon as noticed, raw water might has passed through the membrane side of permeate, fouling this internal layer irreversibly, and producing a gradual increase of the TMP. Neither backwashes, nor CIP operations, were effective. As a result, all the membranes had to be changed and stage IV started on December 14th.

An additional problem related to this pilot plant was that, running at constant aeration during filtration, it produced a lot of foam, requiring the addition of defoamer products and, in consequence, increasing operational costs.

During the first week of January, and under stage IV conditions, the aim was to reach a stable runnability. Firstly, it was decided to work emptying the whole membrane tank during backwashes. Secondly, aeration was performed just the 33% of the filtration time. At the same time, different intervals of time between backwashes were tested to find a compromise between high recovery rates and stable TMP values.

Finally, the demonstration stage V was run with a flux value fixed at 29 L m^{-2} h^{-1} and 65 min was set as the interval between consecutive backwashes. During this stage, membranes showed the same sensitivity as the MF system regarding the peak in iron concentration detected in the feed water on January 22nd; but the system recovered its stability after chemical cleaning. As in the previous case, these episodes of fouling were effectively reversed.

The best chemical cleaning sequence consisted of: (a) performing a daily cleaning at pH 6.5–7.5 with sodium hypochlorite (NaClO) at a concentration of free chlorine of 0.015%; (b) a complementary cleaning with 0.8% citric acid every 3 days; and finally (c) a CIP every 12–14 days combining NaClO at 0.1% free chlorine concentration and NaOH until reaching pH 10.5. This chemical solution was circulated through the membranes for 15 min and then, a soaking period of 240 min was performed. Finally, the solution was rinsed and freshwater was flushed for 2 min.

$N-1$ condition (stage VI, at $J = 33.4$ L m^{-2} h^{-1} and 59 min between backwashes) was tested at the beginning of stage V. The system recovered TMP and permeability after the corresponding chemical cleaning.

LOI and EDX tests showed that fouling, in terms of dry weight, was mainly composed of: SiO_2 (<20%), Fe_2O_3 (>20%), $Ca_3(PO_4)_2$ (>20%) and organic matter of unknown composition (>20%).

3.4. Performance of the S-UF$_B$ plant

Permeability and TMP values before and after the backwashes along this plant trial are shown in Fig. 5. During stage I, TMP and permeability did not show important variations. Backwashes kept the membranes stable. After increasing the flux in stage II (from 34 to 43 L m^{-2} h^{-1}) the system began to perform unstably reaching its limit at −0.70 bar. After this incident, a chemical cleaning was performed to recover TMP and permeability. As 43 L m^{-2} h^{-1} seemed to be too high, a lower value of 38 L m^{-2} h^{-1} was set for stage III, and the time gap between backwashes was also reduced to 25 min. The system continued to show unstable performance even after chemical cleanings were carried out in the system. The situation got worse when the contamination load of the feed water increased on December 5th.

Therefore, the flux fixed for stage IV was set even lower (28 L m^{-2} h^{-1}), and backwashes were carried out every 20 min, however the system did not recovered steady conditions. Therefore, during the demonstration stage (V) the flux was set at 27 L m^{-2} h^{-1}, leaving 23.5 min between backwashes. Stage VI ($J = 36$ L m^{-2} h^{-1} and 15 min between backwashes) started on January 26th, but the system remained unstable before and after

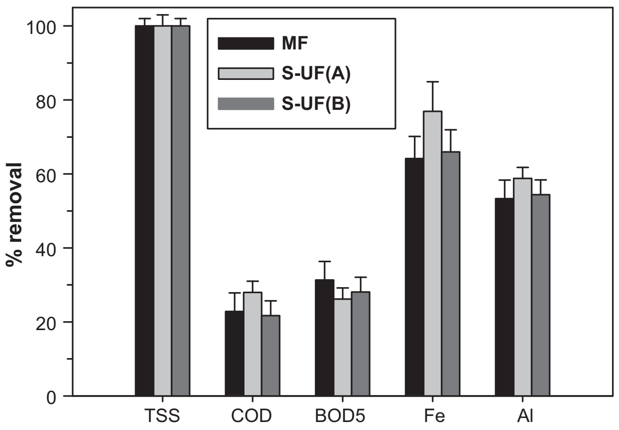

Fig. 6. Comparison of removal efficiencies of TSS, COD, BOD_5, iron and aluminium for the three tested pretreatments.

performing this step. Although backwashes recovered TMP (Fig. 5), the system fouled quickly maintaining unsteady conditions. In fact, after stage VI the system did not recover flux stability again. Chemical cleaning was optimum when treating the membranes: (a) every 8 h with 0.01% NaClO at 35 °C; (b) every 2 days with 0.16% HCl; and (c) performing a weekly CIP combining 0.16% HCl with 0.1% NaClO.

It is remarkable that this plant was more affected by fouling than the others. One main operational difference from $S\text{-}UF_A$ was that the unit worked emptying the whole tank every backwash in stage I. As recovery rate was low, the system began to work with partial drainage of the tank during backwashes from stage II onwards; and a total rinse of the whole tank was performed daily. As result, foulants accumulated inside the tank with time.

Another relevant difference with $S\text{-}UF_A$ was that membranes were not aerated during filtration, which avoided foaming phenomena, but kept attached a higher proportion of foulants on the membranes surface. As a result, these membranes were covered by a certain amount of brown deposit when autopsied. EDX showed that this deposit was mainly formed by: Fe (60%), P (10.9%), Mn (8.6%), Si (4.4%), Al (4.3%), Cl (3.5%), Ca (3.5%), Zn (2.3%), Mg (0.9%) and S (0.6%). FTIR spectra showed the presence of organics and amides. Microbiological examination showed microbial contamination by unicellular bacteria and some slime produced by them. However, microbial contamination was very low in comparison to the presence of iron in the autopsy.

3.5. Overall performance of the pretreatments

The three pilot plants resulted solid enough to produce permeate with a constant high quality regardless the experienced fouling trouble and the high variability of the quality of the wastewater feeding the mWWTP, which was passed after the tertiary treatment and the MF or UF pre-treatments (Table 5). Contaminants removal efficiencies are shown in Fig. 6. The three plants led to a total removal of TSS, and removal efficiencies higher than 20% COD, 25% BOD_5, 65% iron, and 55% aluminium contents.

At the conditions fixed for the demonstration stage (V) of every system, average recoveries of 95% (MF) and 85% (both S-UF) were achieved. All the pretreatments produced permeate with $SDI_{15} < 3$ along all the trial.

3.6. Performance of the RO pilot plants

The evolution of the normalized flux of the permeate for the three RO systems is shown in Fig. 7. All permeate flow rates were kept constant, but feed pressures resulted different among the units, being higher for RO-1 at the beginning of the study. RO-1 and RO-3 evolved in parallel, decreasing their fluxes until the end of November. RO-2 was started up later and it followed the same pattern.

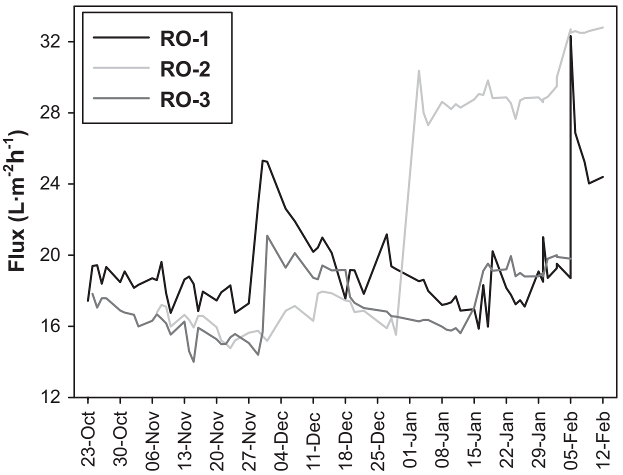

Fig. 7. Flux evolution for the three reverse osmosis pilot plants.

Different chemical cleanings combining HCl/NaOH and Ultrasil10®/NaOH at different temperatures (22–35 °C) and washing times (1–26 h) were applied to RO-1. As it started working at higher pressures, it was more susceptible to fouling. These cleanings seemed to be ineffective, especially when HCl was combined with NaOH. Finally, on November 28th RO-1 and RO-3 were cleaned with the described Ultrasil10®/NaOH combination, and both systems rose their flux over 25 and 21 $L\,m^{-2}\,h^{-1}$, respectively. Ultrasil10® (0.2%)/NaOH and Ultrasil10® (1.5%)/NaOH were used for RO-1 and RO-3, respectively; both cleanings undergone through pH 12 and 1 h of soaking time. Cleaning in RO-1 performed better at 33.0–34.0 °C during 26 h; while cleaning at RO-3 resulted better at 35.5 °C with a washing time of 21 h. Cleanings seemed to be more efficient in RO-1, but it also began to foul faster than in RO-3.

It is important to notice that fluxes after these last effective cleanings were higher than the ones reflected at the beginning of the trial (Fig. 7). This implies that membranes were already fouled when RO systems started to work. This may have been caused by a non-adequate conservation of the membranes under good aseptic conditions while the pretreatments were stabilizing. The type of fouling was mainly organic and biological, since acid chemicals did not have any positive effect when used as cleaning agent. Contrary, after this type of cleaning, both systems showed a decreasing trend of the flux, RO-1 system particularly, which required six chemical cleanings more than RO-3 to keep the flux stable. Despite cleanings, flux never recovered the values of November 28th, which means that fouling was partially irreversible.

As $S\text{-}UF_A$ system started up later, and reported the same unstable flux conditions at which the other two systems were running, it was decided to put new RO-2 membranes, instead of trying to recover the installed ones by performing more chemical cleaning operations. Similar RO membranes from another supplier (B, Table 3) were chosen. At the same time, chloramines began to be dosed after the tertiary basin in this line. In addition, the amount of $NaHSO_3$ dosed before the RO-2 unit was reduced as well. As a result, the flux increased quickly to 30 $L\,m^{-2}\,h^{-1}$, maintaining around 28 $L\,m^{-2}\,h^{-1}$ until February 5th.

On this date a really high dosage of NaClO (150–200 $mg\,L^{-1}$) was accidentally added to the tertiary treatment, leading to free chlorine inflow to the RO membranes during 6 h overnight. The metering pumps placed before the RO units were not adjusted

Table 6
Average water quality after the UV-disinfection step along the trials.

Parameter	Units	RO-1	RO-2	RO-3
pH		5.7	5.8	5.6
Conductivity	$\mu S\,cm^{-1}$	12	9	11
TSS	$mg\,L^{-1}$	<2	<2	<2
Turbidity	NTU	<1	<1	<1
Total COD	$mg\,L^{-1}$	<5	<5	<5
BOD_5	$mg\,L^{-1}$	<2	<1	<1
Sulphates	$mg\,L^{-1}$	<3	<3	<3
Dissolved silica (as SiO_2)	$mg\,L^{-1}$	<0.2	<0.2	0.2
Chlorides	$mg\,L^{-1}$	<3	<3	<3
Hardness	$mgCaCO_3\,L^{-1}$	<7	<7	<7
Calcium	$mgCa\,L^{-1}$	<1	<1	<1
Magnesium	$mg\,L^{-1}$	<1	<1	<1
Bicarbonates	$mg\,L^{-1}$	<5.0	<5.0	<5.0
Iron	$mg\,L^{-1}$	<0.01	<0.01	<0.01
Aluminium	$mg\,L^{-1}$	<0.01	<0.01	<0.01
Manganese	$mg\,L^{-1}$	<0.06	<0.06	0.06
Ammoniacal nitrogen	$mgN\,L^{-1}$	<0.05	<0.05	<0.05
Nitrates	$mgNO_3\,L^{-1}$	0.69	0.23	0.24
Phosphorous	$mgP\,L^{-1}$	0.07	0.06	0.06
Microorganisms	$CFU\,100^{-1}\,mL^{-1}$	<1	<1	<1

to dose enough $NaHSO_3$ to buffer this amount of free chlorine and prevent its arrival to RO membranes. As a result, all the fouling deposited on the membrane surface was totally cleaned, and permeate fluxes of RO-1 and RO-2 reached $\approx 33\,L\,m^{-2}\,h^{-1}$. Most polyamide membranes can tolerate $1\,mg\,L^{-1}$ of free chlorine exposure during 200–1000 h before increasing their permeate flux and noticing a reduction of salt rejection [45]. If the membranes were damaged by this chemical, it should have been noticed in the subsequent performed autopsies, as it is described next. RO-3 was not affected by free chlorine because the line was stopped at that moment.

Regardless the reported troubles found along the trials, the average final water quality produced along the whole trial in each line after the UV-disinfection units was high, as shown in Table 6. By far, water quality not only met the requirements to be used within HPM mill, but also the requirements set by the Spanish legislation [49], the USEPA regulations [50] and the WHO guidelines [51] for drinking water (Table 1). Moreover, it also met the quality requirements of NEWater [52]. The pH value does not fulfil any of these guidelines because the water out-flowing the UV-disinfection units had not been stabilized yet, and a pH adjustment step with lime or sodium hydroxide should be performed afterwards to avoid the corrosive character of water.

3.7. *Autopsies of the RO membranes*

RO membrane elements of stages 1 and 4, from both suppliers, were autopsied in every line. Fujiwara tests were positive for all RO-1 and supplier B's RO-2 membranes, indicating that they were exposed to free chlorine. On the other hand, dye tests were negative for all the membranes. Moreover, their performance was within the designed values of salt rejection, indicating that the free chlorine peak did not cause a significant oxidative damage to the membranes. But if the exposure to free chlorine would have continued for a few more hours, membranes may have been surely degraded [45].

3.7.1. *RO-1 membranes analyses*

The autopsied RO membrane element of stage 1 resulted slightly fouled with a layer of soft grey slimy gelatine. Correspondingly, the element of stage 4 showed a lower foulant content of same characteristics. Dried solids density of the first one resulted $0.18\,mg\,cm^{-2}$, while it accounted for less than $0.10\,mg\,cm^{-2}$ on the latter. Foulant composition was very similar in both, mainly biofouling, and only small amounts of inorganic materials like silica, phosphorous, sulphur and calcium; all present as oxides, with a content of around 1% each.

3.7.2. *RO-2 membranes analyses*

Regarding the membranes delivered by supplier A, the first element was fouled with a soft brown gelatinous deposit spread over the whole surface. The autopsied fourth element was also slightly less fouled with a similar gelatinous deposit. Foulant composition was mostly of organic nature, including both biofouling and soluble organics like hydrocarbons and silicone oils. In addition, low quantities of phosphorous as P_2O_5 (4%), calcium as CaO (1%), and sulphur as SO_3 (1%) were also present. Some iron, as Fe_2O_3, content (1%) was also detected on this fourth element. These soluble organics, phosphates and sulphates serve as food source for bacteria, thus promoting biogrowth [53]. In fact, sulphate-reducing bacteria were found on the membrane surface.

Membranes from supplier B appeared very clean. They only showed some spaced imprints and a few scattered spots of organic material. Very fine aggregates rich in iron content were also detected locally. Several particles of 50–150 μm were found with the appearance of a thin film. Why these modules were less fouled, and biofouling was effectively fought against, in comparison to the other RO membranes tested, may be attributed to the use of chloramines, although the fact that they worked for just 1 month may have some relevance as well.

3.7.3. *RO-3 membranes analyses*

These modules were considerably fouled with a layer of brown deposit of a density of $0.22\,mg\,cm^{-2}$ for the first element, and $0.10\,mg\,cm^{-2}$ for the fourth one. Foulant composition was similar to the RO-1 and RO-2 membranes delivered by the same supplier (A, Table 3), including sulphate-reducing bacteria. Main inorganic content was iron as Fe_2O_3 (9–14%), phosphorous as P_2O_5 (8–6%), and calcium as CaO (2–3%). Smaller amounts of silicon (as SiO_2), sulphur and chlorine were also present at contents of ≈1%.

3.8. *Chemical cleaning of RO systems*

Different combinations of chemicals and conditions were tested with the autopsied elements in order to find the best cleaning procedure to remove the above reported fouling. As a result, two alternatives were found as the best cleaning procedures:

(a) 4% (v/v) solution of PermaClean® PC-98 at pH 11.5 and $T = 30–35\,^{\circ}C$, for 2 h + 4% (v/v) solution of PermaClean® PC-77 at pH 3.8, and $T = 20–25\,^{\circ}C$, for another 2 h.
(b) 1% (v/v) solution of PermaClean® PC-67 + 2% (v/v) solution of PermaClean® PC-33 at pH 11.5, and $T = 30–35\,^{\circ}C$, for 2 h.

4. Overall performance of the trials: technical recommendations and lessons to be learnt

An adequate control of the tertiary treatment in the mWWTP previous to the tested membrane filtration system is critical to the success of these reclamation systems, particularly if the amount of industrial wastewater dumped to the mWWTP is high, which produces uncontrolled spilling of foulants and instability of the overall process. Therefore, appropriate pretreatments and management operations and spilling control measurements should be designed, especially during long weekends and holidays.

A high load of industrial wastewater makes the water reclamation process difficult because its quality varies due to changes in the production processes. The presence of different products associated to certain production stages, or cleaning operations during the stops of production in the mills, highly influence the quality of the treated water and promote an enhanced membrane fouling. Special care must be taken during long weekends and holidays periods, when intense cleaning operations may be performed taking advantage of the stop of the machines. Further research identifying problematic products and looking for alternative solutions must be supported in time.

The absence of any residual halogen in the feed water should be particularly monitored for RO units. As the oxidative effect of free chlorine is catalyzed by the presence of iron and other transition metals present in the foulant layer, the content of these elements should be also monitored and controlled thoroughly.

A constant disinfection of MF and UF systems was necessary to avoid biofouling. Chloramines provided an efficient disinfection of RO polyamide membranes with a better performance than free chlorine.

Furthermore, dead-end zones and corners are places susceptible for the fast growth of microorganisms due to the absence of turbulent flow and light. Furthermore, these are places difficult to access by biocides and cleaning chemicals. Therefore, these zones should be avoided as much as possible or limited in the design of systems similar to the ones implemented in this initiative. In addition, designers should also consider that, as the longer the pipes are, the higher biogrowth will be potentially developed.

The optimization of the operating costs is based on technical issues. That is, while pressurized systems run at higher pressures implying greater pumping costs, submerged systems require a greater investment on aeration, and recovery rates are also lower. These costs also include other factors, such as water quality, flux, systems recovery, type of pretreatment; and costs of labour and consumables.

From this experience, running under constant aeration conditions in the submerged systems reduces the trouble caused by fouling, but it may also produce an increase of the pH of the permeate, due to a fast CO_2 removal, and led to additional foam problems.

As the pressurized system worked running more frequent backwashes, its performance resulted more stable. The submerged system required more time between backwashes to keep a high recovery, so it was more susceptible to be affected by fouling.

The selection of suited chemical agents and time gaps between cleaning operations resulted to be the key to keep a good performance of all the types of membrane systems. Furthermore, temperatures at which the membranes are cleaned, and soaking times, are parameters of main importance to be defined, particularly when optimizing RO chemical cleanings.

5. Conclusions

An adequate management of the tertiary treatment at the mWWTP, constant disinfection, an appropriate design of the plants, and a good performance of cleaning operations were very important factors to be considered when implementing this type of reclamation initiatives.

After optimizing the operating conditions in these trials, all the pretreatments showed a turbidity reduction of 95%, and a recovery higher than 85%, producing a similar water quality (SDI < 3).

The removal of microorganisms was guaranteed to less than $1\,\mathrm{CFU}\,100^{-1}\,\mathrm{mL}^{-1}$ in RO stage; and the percentages of salt rejection were kept above 99%. Total COD in the permeate was always below the detection limit ($<5\,\mathrm{mg\,L}^{-1}$).

Results show that the water quality achieved with the tested double membrane system is adequate to substitute fresh water in a paper mill. A wastewater reclamation plant is currently being built in Madrid based upon the results of this initiative; HPM will be the first mill producing 100% recycled paper using 100% reclaimed water.

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