DOCTORAL THESIS

SUBSTITUTION OF CONVENTIONAL PRE-TREATMENT UNITS BY MEMBRANE BASED PROCESSES IN DRINKING WATER TREATMENT

DOCTORAT EN ENGINYERIA DE PROCESSOS QUÍMICS

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Als meus pares

ABSTRACT

This thesis focused on the feasibility of substituting drinking water treatment plant (DWTP) conventional pre-treatment by ultrafiltration (UF). For such purpose, bench and pilot scale tests with natural water were conducted, first, to address the technical feasibility and, second, to optimize its performance in order to determine whereas the proposed scheme was competitive from hydraulic and quality perspectives with the current conventional pre-treatment.

Tailored microbes based tests were defined to assess direct UF proper functioning and reliability. Additional advantages related to direct UF besides those purely related to the pre-treatment unit were investigated: the effects on reverse osmosis (RO) physico-chemical and transport properties caused by the exposure of certain chemicals.

The case study selected was Sant Joan Despí DWTP (Barcelona, Spain) due to its particularities: it treats Llobregat River water, which is a highly variable water resource in terms of quality and quantity, and it is a complex multi-stage system.

Keywords

Ultrafiltration, drinking water treatment plant, pre-treatment, fouling, efficiency, integrity, reverse osmosis, degradation

Preface

Numerous drinking water treatment plants (DWTPs) will face a complex scenario in the upcoming decades: an increasing water demand will have to be satisfied using lower quantity and quality primary resources. In addition to this, legislation, increasing energy cost and social requirements in terms of process sustainability will also shape how DWTP should be.

In order to meet these requirements, DWTPs will have to adapt their current treatment schemes to become more efficient from technical, economic and environmental perspectives. DWTPs conventional pre-treatment, typically composed of coagulation-flocculation, settling and sand filtration, presents some limitations, such as high chemical consumption and thus sludge generation, significant space requirements, increased water losses, etc. Membrane technology has quickly evolved during the last decades, presenting nowadays an enhanced performance and diminished costs. In particular, low pressure membranes (microfiltration (MF) and ultrafiltration (UF)) application has significantly increased within the drinking water treatment scheme.

As a result, this thesis focused on the feasibility of substituting, partially or totally, DWTPs conventional pre-treatment by membrane based units. For such purpose, bench and pilot scale tests with real water were conducted, first, to address the technical feasibility and, second, to optimise the performance in order to determine whereas the proposed scheme was competitive from hydraulic and quality perspectives with the current conventional pre-treatment. The case study selected was Sant Joan Despí (SJD) DWTP (Barcelona, Spain) due to its particularities: it treats Llobregat River water, which is a highly variable water resource in terms of quality and quantity, and it is a complex multi-stage system. As a result, this study covered a wide range of conditions and also the technology under consideration could be pushed to its limits, so that if it proved to be successful within this framework, probably it would be applicable in many other case studies.

Initially, a bench scale UF membrane unit was assessed as a potential substitute of sand filtration, a part of the conventional pre-treatment. The water quality produced by the UF membrane was equivalent to the conventionally treated one and the UF membrane was able to work continuously. Fouling, which is the accumulation of retained substances on membrane surface and implies the need of undertaking cleaning operations, is a main drawback in membrane based processes. The parameters affecting the backwash efficiency and the fouling reversibility were studied in detail, in order to better understand how to optimise the system. Also the organic fractions retained by the UF membrane and released during different cleaning operations were quantified. Due to the successful results obtained of a partial substitution of the conventional pre-treatment, a pilot plant equipped with a full scale commercially available UF module was evaluated as an alternative to the whole conventional pre-treatment from SJD DWTP. Raw river water was directly filtered by UF and by dioxichlorination, coagulation-flocculation, settling and sand filtration in parallel in order to compare both treatment schemes under the same conditions. The two year testing period enabled the definition of the optimal conditions of the proposed scheme (direct UF), quantifying its hydraulic, physico-

chemical and microbiological performance and comparing it to the conventional pre-treatment. The system proved to be able to work continuously, regardless the quality of the feed water, whereas the conventional pre-treatment was stopped when turbidity was above 500 – 1,000 NTU (under normal and water scarcity conditions respectively). The highest water yields (ratio between net permeate produced and intaken water) achieved ranged between 94.0% - 94.7% in optimal conditions, involving one or two chemically enhanced backwashes (CEBs) per day, transmembrane pressure (TMP) below 1 bar and filtration fluxes of 40 – 70 L/(m^2·h). Reagents consumption per cubic meter of feed water was 0.6 – 2.1 mL NaOH/m^3, 1.2 – 4.3 mL NaClO/m^3, 2.5 – 8.6 mL HCl/m^3 (CEBs) and 0 – 1.5 mg Fe(III)/L of ferric chloride (micro-coagulation). These values were competitive with the current conventional pre-treatment.

When a micro-coagulation (dose < 1.5 mg Fe(III)/L) previous to the UF was applied, the increase of the hydraulic resistance during filtration was decreased and stabilised. This effect was particularly noticeable in winter (average temperature 8.9 ºC), when the attainable filtration flux could be increased from 40 L/(m^2·h) to 70 L/(m^2·h), enabling the implementation of the same filtration flux through the year. Moreover, the performance of a micro-coagulation led to an increase in the hydraulic cleaning efficiency and to a decrease of the CEBs frequency.

In terms of pre-treated water quality, most of the physico-chemical parameters monitored presented lower values and variability in the direct UF scheme than in the conventional pre-treatment process: turbidity (0.068±0.004 vs. 0.313±0.031 NTU), TSS (0.92±0.17 vs. 1.03±0.16 mg/L), SDI_{15} (1.90±0.15 vs. 5.20±0.13 %/min), $MFI_{0.45}$ (0.85±0.73 vs. 25.18±11.35 L/s^2), DOC (3.77±0.16 vs. 3.51±0.19 mg/L) and UV_{254} (0.0815±0.0018 vs. 0.0725±0.0028). From a microbiological perspective, the direct UF scheme tested ensured the average removal of > 5 log_{10} units of bacteria and viruses greater than 60 nm. In the case of microbes of this size, the performance of the assessed UF membrane (PVDF pore size 40 nm) significantly outperformed that of the dioxichlorination, coagulation/flocculation, settling and sand filtration pre-treatment, presenting greater removal values and lower variability. In contrast, the direct UF scheme only guaranteed a 3 log_{10} units removal of viral indicators and viruses whose sizes were lesser than 40 nm. Microbes of this size were removed to a larger extent by the DWTP conventional pre-treatment than that of the direct UF membrane assessed, although not always significantly. According to the results obtained, the removal of the microbiological parameters assessed did not depend on their feed water concentration, analogously to the majority of the physico-chemical parameters assessed. The fact that the water quality produced by direct UF was equal or superior to the conventionally pre-treated one for most of the parameters addressed would have a positive impact in the subsequent reverse osmosis (RO) unit, reducing the cleaning requirements and extending its lifetime.

The implementation of direct UF would imply the pre-treatment being a single membrane filtration step. This has advantages in terms of process complexity, space requirements, as well as avoidance of chemical based disinfectants dosage. Nevertheless, the preservation of its separating properties along time is of utmost importance, especially from a microbiological standpoint, to protect public health from microbiological risk. Drinking Water Guidelines from

the World Health Organisation (WHO) emphasise the need to manage and assess the risk of the product water to safeguard its quality by Water Safety Plans (WSP) means and thus, avoid outbreaks of waterborne disease which still occur in both developed and developing countries. Consequently, microbes based tailored tests aiming at assessing membrane integrity were defined and conducted periodically, to determine the removal capacity reliability of the pre-treatment scheme proposed in this thesis. *Bacillus* sp. spores and bacteriophage PDR-1 appeared as suitable microbes for such purpose. Results showed that membrane integrity had not been compromised despite the challenging conditions that direct UF posed.

Besides the economic savings of decreasing the reagents dosage with the envisaged scheme and the increased RO membrane lifetime due to the improved water quality delivered by direct UF, additional benefits to the whole treatment system would be experienced. When multi-stage processes are in place, their functioning can affect each other, so that careful harmonisation and control of water chemistry is needed. For instance, RO is sensitive to certain compounds, such as chlorine, aluminium, etc. Therefore, modifying the pre-treatment, and especially stopping or decreasing the dosage of certain chemicals, may have an impact on RO membranes physico-chemical and/or transport properties. Currently, membrane degradation is a main challenge among RO thin film composite membranes. Lab research was conducted to identify additional benefits associated to direct UF, like the avoidance of the initial dioxichlorination and thus, the chlorite presence and the corresponding bisulphite addition to reduce it. A catalytic effect between iron(III) and bisulphite was identified, which resulted in a significant drop in chloride rejection, which was caused by an increase in the fraction of aggregate pores and in the size of network pores of the RO membrane. This process was fast and did not provoke major changes in terms of membrane composition under the conditions assessed. Iron(III), from coagulation, also enhanced the incorporation of bromine in the membrane when dosed in chlorite and bromide containing solutions. This turned into an increased water flux and chloride passage under the conditions assessed, being the latter a time dependent process, with greater values under longer exposure time. With the implementation of direct UF some of the RO degradation scenarios identified would be minimised, resulting into further advantages for DWTPs.

Based on the results obtained, direct UF could be a feasible alternative to conventional pre-treatment. The main advantages associated to this configuration would be the significant decrease in chemical consumption (initial disinfectant, coagulants/flocculants and RO cleaning agents mainly) and sludge production, increased water quality produced, extended RO lifetime, decreased space requirements, compactness of the treatment scheme and low space requirements, easiness of automation and avoidance/minimisation of chemical disinfectants often linked to the formation of disinfection by-products (DBPs).

Thesis organisation

This thesis addressed the substitution of conventional pre-treatment units by low pressure membrane based processes in DWTPs, assessing its feasibility and quantifying its advantages and limitations. Low pressure membranes have proved to be efficient systems for water treatment, presenting remarkable advantages such as high and stable water quality, low reagents need and small footprint. These benefits may contribute to the fulfilment of more strict pieces of legislation and to face upcoming challenges in terms of water scarcity, energy efficiency and environment protection. The need to quantify their capabilities and assess their feasibility motivated this thesis.

An introduction on the use of membranes in drinking water treatment, and particularly of direct UF, the alternative pre-treatment scheme mainly addressed within this thesis, was performed in **Chapter 1**. **Chapter 2** confirmed the feasibility of partially substituting the conventional pre-treatment by low pressure membranes in SJD DWTP. In particular, UF proved to be a suitable alternative to sand filtration, producing water whose quality was equal or superior to the one treated by conventional sand filtration. The backwash parameters affecting the fouling reversibility were addressed, in order to optimise them. **Chapter 3** went a step further and tested the viability of substituting the whole conventional pre-treatment: an initial disinfection, coagulation/ flocculation, settling and sand filtration by direct UF. Results proved the feasibility to directly treat raw river water of challenging characteristics (e.g. turbidity ranging from 5 to >1,000 NTU) continuously, without the need to stop the process even when extreme episodes, like flash flood events, occurred. Such scheme demonstrated the capacity to treat low quality water sources, which otherwise would not be treated by the conventional pre-treatment. The quality of the product water was high regardless of incoming water quality fluctuations. **Chapter 4** explored the hydraulic sustainable conditions (e.g. filtration flux, filtration duration, cleaning operations frequency) achievable in different scenarios (winter / summer, coagulation / no coagulation), determining the reagents needs, cleaning demands and pressures required. The effects of micro-coagulation in direct UF were studied since it enabled implementing harsher operational conditions, especially during winter time. Membrane resistance increase during each filtration cycle was smaller and hydraulic cleaning became more effective when micro-coagulation was in place. Micro-coagulation enabled the implementation of similar operational conditions through the year, which would lead to a simpler design of a DWTP.

Because of the demanding conditions direct UF implies, membrane integrity becomes of utmost importance, since its compromise may cause the loss of filtration properties. **Chapter 5** defined a protocol to address membrane integrity by tailored tests based on various microorganisms. It was verified with the three existing UF configurations (submerged outside-in, pressurised outside-in and pressurised inside-out). **Chapter 6** went a step further and reported the results of the two years of operation of the direct UF scheme at pilot level, and contrasted these integrity tests with other microbiological analyses routinely performed in the feed and permeate streams. This complemented the operational and physico-chemical characterisation of direct UF from the previous chapters (3, 4) with microbiological assays.

Chapter 7 was devoted to one of the impacts of implementing direct UF on the subsequent stage of a DWTP, the RO unit: the avoidance of the initial dioxichlorination. Indeed, the adoption of direct UF enables eliminating the initial disinfection stage of the treatment process. This means that the potential of facing chlorine based species in the RO is lowered, only caused by the hypochlorite dosed during UF cleaning operations. As a result, the dosage of bisulphite could be significantly reduced and, as shown, RO membranes degradation might be minimised. Also the impact in terms of RO membrane integrity of reducing/eliminating coagulants dose in the pre-treatment, as envisaged within direct UF scheme, was addressed.

Chapter 8 summarised the results obtained and suggested further research based on the findings of this study. This thesis addressed not only the feasibility and characterisation of the direct UF performance, but also the impacts it may have on other stages of DWTPs. Indeed, it determined the effects of several compounds on RO membrane composition and performance which had not been characterised before, providing new insights into the field through the use of advanced techniques. As a result, this thesis provides tools for plant operators to optimise direct UF performance if implemented and means to address its functioning, and novel results for scientific community on RO degradation.

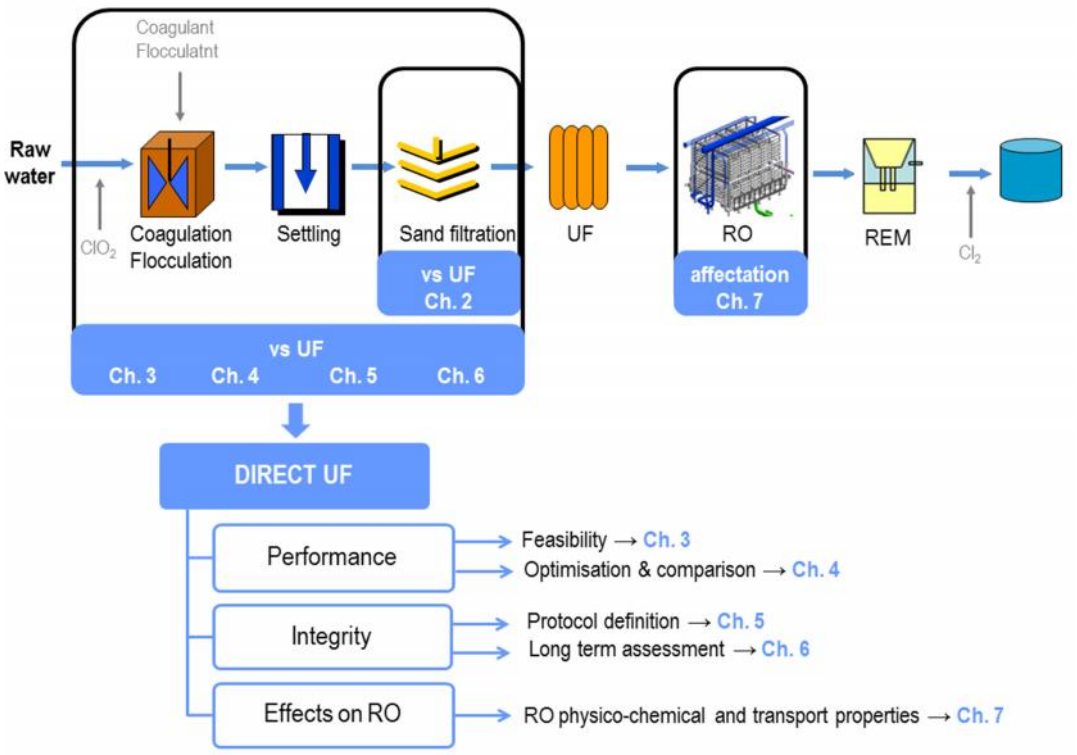

Figure 0.1. Graphical summary of this thesis organisation. Ch: chapter, REM: remineralisation.

Figure 0.1 graphically summarises this thesis organisation. It represents a DWTP equipped with RO membranes and the topics addressed in Chapter 2, 3, 4, 5, 6 and 7 are placed below the unitary processes they are related to. Chapter 1, introduction, and Chapter 8, conclusions and outlook, are not depicted since they present a holistic approach. Regarding the four chapters devoted to direct UF, the aim of each one is detailed to clearly differentiate them and remark the progressive approach adopted.

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Conducting a PhD is a complex labour which requires the inputs of several people in different ways. Often repeating tests and re-designing the experimental plan is needed, because as Antonio Machado stated: *traveller there is no path; a path is made by walking (caminante no hay camino, se hace camino al andar)*. Indeed, this is the beauty and the struggle of a doctoral thesis, and so the chance to interact with different co-workers to face multiple challenges. Therefore, I would like to thank here all those colleagues, friends and relatives who somehow have helped me, supported me and kept faith in me and my research during this four year journey.

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Finally, my deepest acknowledgement is for my family, who has transmitted me the values, attitudes and behaviour needed not only to successfully accomplish this PhD but to face life challenges. Especially, infinite thanks to my parents, who have unconditionally supported me during this thesis and with whom I will always be indebted.

CONTENT

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Abbreviations and symbols

Chapter 1

AB	Aigües de Barcelona
BW	backwash
CA	cellulose acetate
CEB	chemically enhanced backwash
CFU	colony forming unit
CPU	central processing unit
DBP	disinfection by-product
DMF	dual media filter
DOC	dissolved organic carbon [mg C/L]
DWTP	drinking water treatment plant
EC	European Commission
EU	European Union
GAC	granular activated carbon
HACCP	hazard analysis and critical control point
HRT	hydraulic retention time [min]
MF	microfiltration
MPN	most probable number
N.A.	non applicable
NF	nanofiltration
NOM	natural organic matter
PAC	powder activated carbon
PACl	polyaluminium chloride
PES	polyethersulfone
PP	polypropylene
PS	polysulfone
PVDF	polyvinyl difluoride
RBS	Rutherford Backscattering Spectroscopy
REM	remineralisation
RO	reverse osmosis
RT-PCR	real time polymerase chain reaction
SDI_{15}	silt density index [%/min]
SJD	Sant Joan Despí
TFC	thin film composite
TMP	transmembrane pressure
TOC	total organic carbon [mg C/L]
UF	ultrafiltration
UV_{254}	absorbance at 254 nm [cm^{-1}]
WSP	water safety plans
WHO	World Health Organisation

Chapter 2

BB	building blocks [µg C/L]
BP	biopolymers [µg C/L]
BW	backwash
BW_{CEB-c}	chemically enhanced backwash composition
BW_d	backwash duration
BW_f	backwash frequency
BW_{TMP}	backwash transmembrane pressure
CEB	chemically enhanced backwash
CIP	cleaning in place
CIP-A	acid cleaning in place
CIP-B	alkaline and oxidant cleaning in place
DOC	dissolved organic carbon [mg C/L]
DOM	dissolved organic matter [mg C/L]
HPSEC	high performance size exclusion chromatography
HS	humic substances [µg C/L]
J	permeate flux [$m^3/(m^2 \cdot s)$]
LMWA	low molecular weight acids [µg C/L]
LMWN	low molecular weight neutrals [µg C/L]
MF	microfiltration
MW	molecular weight
MWCO	molecular weight cut off
OC	organic carbon
$R^i_{after\ BW}$	resistance after the BW of the filtration cycle "i" [m^{-1}]
$R^i_{before\ BW}$	resistance before the BW of the filtration cycle "i" [m^{-1}]
$R_{fouling}$	resistance due to the total fouling [m^{-1}]
R_{irrev}	resistance due to the irreversible fouling [m^{-1}]
R_m	resistance of clean membrane [m^{-1}]
R_{rev}	resistance due to the reversible fouling [m^{-1}]
R^i_{rev}	resistance due to the reversible fouling in the filtration cycle "i" [m^{-1}]
R_{total}	total resistance of the fouled membrane [m^{-1}]
TMP	transmembrane pressure [bar]
TOC	total organic carbon [mg C/L]
UV_{254}	absorbance at 254 nm [cm^{-1}]
Δp	transmembrane pressure [bar]
µ	viscosity [bar·s]

Chapter 3

A	membrane area [m^2]
CEB	chemically enhanced backwash
DOC	dissolved organic carbon [mg C/L]
DWTP	drinking water treatment plants
EPS	extracellular polymeric substances
HC	hydraulic cleaning
MF	microfiltration
NF	nanofiltration
NOM	natural organic matter
R	membrane resistance [m^{-1}]
R_n	membrane resistance before cleaning operation [m^{-1}]
R_{n+1}	membrane resistance after cleaning operation [m^{-1}]
RO	reverse osmosis
SDI_{15}	silt density index [%/min]
TEP	transparent exopolymer particles
TSS	total suspended solids [mg/L]
UF	ultrafiltration
V	filtered volume [m^3]
v	specific volume [m]
α	specific cake resistance [m^{-2}]

Chapter 4

A	membrane area [m^2]
BB	building blocks [µg C/L]
BP	biopolymers [µg C/L]
CEB	chemically enhanced backwash
DOC	dissolved organic carbon [mg C/L]
DWTP	drinking water treatment plant
HC	hydraulic cleaning
HOC	non-chromatographic fraction of DOC
HPSEC	high performance size exclusion chromatography
HS	humic substances [µg C/L]
J	water flux [$L/(m^2 \cdot h)$]
LMWA	low molecular weight acids [µg C/L]
LMWN	low molecular weight neutrals [µg C/L]
$MFI_{0.45}$	modified fouling index [s/L^2]
MPN	most probable number
MW	molecular weight
PES	polyethersulfone
R	hydraulic membrane resistance

RO	reverse osmosis
SCADA	supervisory control and data acquisition
SDI_{15}	silt density index [%/min]
TMP	transmembrane pressure
TOC	total organic carbon [mg C/L]
TSS	total suspended solids [mg/L]
UF	ultrafiltration
UV_{254}	absorbance at 254 nm [cm^{-1}]
V	filtered volume [m^3]
v	specific volume [m]
α	specific cake resistance [m^{-2}]

Chapter 5

BW	backwash
CEB	chemically enhanced backwash
C_f	surrogate concentration of the bulk feed solution [CFU/mL or PFU/mL]
C_p	surrogate concentration of the bulk permeate solution [CFU/mL or PFU/mL]
CFU	colony forming unit
DWTP	drinking water treatment plant
ETV	Environmental Technology Verification
IESWTR	Interim Enhance Surface Water Treatment Rule
IOS	International Organization for Standardization
LRV	logarithmic removal value
LRV_t	logarithmic removal value (theoretical)
LT1ESWTR	Long Term 1 Enhanced Surface Water Treatment Rule
LT2ESWTR	Long Term 2 Enhanced Surface Water Treatment Rule
MCF	membrane cartridge filtration
MF	microfiltration
NF	nanofiltration
UF	ultrafiltration
PDT	pressure decay test
PFU	plaque forming unit
Q_{breach}	breach flow [L/min]
Q_p	permeate flow [L/min]
RO	reverse osmosis
SWTR	Surface Water Treatment Rule
TMP	transmembrane pressure [bar]
US EPA	United Stated Environmental Protection Agency
VCF	volumetric concentration factor
WHO	World Health Organisation

Chapter 6

CEB	chemically enhanced backwash
C_f	microorganism concentration in the feed
CFU	colony forming unit
C_p	microorganism concentration in the permeate
DOC	dissolved organic carbon [mg C/L]
DWTP	drinking water treatment plant
ENT1	infectious enteroviruses [PFU/L]
ENT2	genome copies of enteroviruses (NoV GI and NoV GII) [GC/L]
ENT	enteroviruses
ENTPFU	no infectious enteroviruses
FRNAPH	F-specific RNA bacteriophages [PFU/L]
GC	genome copies
LMH	$L/(m^2 \cdot h)$
LRV	logarithmic removal values
MF	microfiltration
$MFI_{0.45}$	modified fouling index [s/L^2]
NOR	noroviruses
NoV GI	noroviruses of genotype I [GC/L]
NoV GII	noroviruses of genotype II [GC/L]
PCR	polymerase chain reaction
PFU	plaque forming units
PVDF	polyvinylidene difluoride
q-RT-PCR	quantitative real time polymerase chain reaction
RO	reverse osmosis
SDI_{15}	silt density index [%/min]
SJD	Sant Joan Despí
SOMCPH	somatic coliphages [PFU/L]
SSRC	spores of sulfite-reducing clostridia [CFU/L]
TMP	transmembrane pressure [bar]
TSS	total suspended solids [mg/L]
UF	ultrafiltration
UV_{254}	absorbance at 254 nm [cm^{-1}]

Chapter 7

A	product water permeation coefficient [$m^3/(m^2 \cdot d \cdot MPa)$]
A_0	product water permeation coefficient of the virgin membrane [$m^3/(m^2 \cdot d \cdot MPa)$]
B	solute permeation coefficient [m/d]
B_0	solute permeation coefficient of the virgin membrane [m/d]
C_f	solute concentration of the bulk feed solution [M]
C_w	solute concentration of feed solution next to the membrane wall [M]

C_p	solute concentration of permeate solution [M]
J_s	solute flux [mol/(m^2·d)]
J_v	water flux [m^3/(m^2·d)]
TFC	thin film composite
PA	polyamide
P_f	hydraulic pressure of the feed solution [MPa]
p_p	hydraulic pressure of the permeate solution [MPa]
RBS	Rutherford Backscattering Spectroscopy
RO	reverse osmosis
R-WT	rhodamine-WT
SMBS	sodium metabisulphite
α	fraction of the total product water flux corresponding to advection
Δp	hydraulic pressure difference across the membrane active layer [MPa]
$\Delta\pi = (\pi_w - \pi_p)$	osmotic pressure difference across the membrane active layer [MPa]
π_p	osmotic pressure of the permeate solution [MPa]
π_w	osmotic pressure of feed solution next to the membrane wall [MPa]

Chapter 8

BB	building blocks [µg C/L]
BP	biopolymers [µg C/L]
CEB	chemically enhanced backwash
CFU	colony forming unit
DOC	dissolved organic carbon [mg C/L]
DWTP	drinking water treatment plant
ENT1	infectious enteroviruses [PFU/L]
ENT2	genome copies of enteroviruses (NoV GI and NoV GII) [GC/L]
GC	genome copies
HC	hydraulic cleaning
HS	humic substances [µg C/L]
LMWN	low molecular weight neutrals [µg C/L]
LoQ	limit of quantification
$MFI_{0.45}$	modified fouling index [s/L^2]
MPN	most probable number
NoV GI	noroviruses of genotype I [GC/L]
NoV GII	noroviruses of genotype II [GC/L]
PFU	plaque forming unit
RO	reverse osmosis
SDI_{15}	silt density index [%/min]
SOMCPH	somatic coliphages [PFU/L]
TSS	total suspended solids [mg/L]
UF	ultrafiltration
UV_{254}	absorbance at 254 nm [cm^{-1}]

Note: in some cases non international system units were used because the implemented ones are more widely used among membrane manufacturers and plant operators and thus, given values may be more meaningful for such readers. In particular:

Parameter	International system unit	Used units	Conversion between used units and international system units
Chemical concentration	M	mg/L or µg/L	/(MW·1E^{+3}) or /(MW·1E^{+6}) respectively
Hydraulic retention time	s	min	*60
$MFI_{0.45}$	s/m^6	s/L^2	*1E^{+6}
Product water permeation coefficient (A)	$m^3/(m^2 \cdot s \cdot Pa)$	$m^3/(m^2 \cdot d \cdot MPa)$	/8.64E^{+10}
SDI_{15}	%/s	%/min	/60
Solute flux (J_s)	$mol/(m^2 \cdot s)$	$mol/(m^2 \cdot d)$	/8.64E^{+4}
Solute permeation coefficient (B)	m/s	m/d	/8.64E^{+4}
Transmembrane pressure	Pa	bar	*1E^{+5}
UV_{254}	m^{-1}	cm^{-1}	*1E^{+2}
Water flux	$m^3/(m^2 \cdot s)$	$L/(m^2 \cdot h)$ or $m^3/(m^2 \cdot d)$	/3.6E^{+6} or /8.64E^{+4} respectively

MW: molecular weight (g/mol)

CHAPTER 1

Introduction

Abstract

The substitution of conventional pre-treatment units by membrane based processes in drinking water treatment is motivated by the limitations of conventional pre-treatment units to face upcoming water challenges and by the advantages that membrane processes present, which may contribute to their successful achievement. A review of the current limitations of conventional pre-treatment in drinking water treatment plants (DWTPs), the application and advantages of low pressure membranes within the water sector, previous experiences reported assessing the feasibility of substituting conventional pre-treatment by direct ultrafiltration (UF) as well as the description of the case study was conducted. This chapter is thus, a brief introduction to this thesis and outlines its objectives and methodological approach.

1.1. Water scarcity

Water access is fundamental for human life, since it is necessary for health, sanitation, ecosystems, agriculture, livestock, industry, etc. Freshwater only accounts for 2.5% of the worlds water, being solely 1% easily accessible (UNESCO). Currently, freshwater scarcity has become a major concern in many arid and semi-arid countries worldwide to such an extent that water supply for meeting current and future demands is one of the main challenges for mankind (Fritzmann et al., 2007, UNESCO, 2009). According to United Nations, 1.2 billion people, so nearly one fifth of world population, live in areas of physical water scarcity and 500 million people are reaching this situation. Another 1.6 billion inhabitants are in economic water scarcity, which means that infrastructures to uptake water from rivers and aquifers is lacking. It is estimated that by 2025 the number of people living in areas with absolute water scarcity will raise to 1.8 billion and two-thirds of the world population could suffer water stress (United Nations, 2013).

Figure 1.1 depicts the water stress calculated as the percentage of water withdrawal compared to the total available water, in 1995 and in 2025 (projected). As can be seen, the global water stress estimated in 2025 is higher than in 1995 because the number of regions under water scarcity and the severity of the water stress increase. In particular, areas with low precipitation and/or with high population density are the most affected. Several factors drive this water scarcity context, including increasing demand due to continued population growth and new consumption patterns, industrial development, dependence on single supply sources, depletion and pollution of groundwater as well as hydrological and climate changes, among others (Bixio et al., 2006, Verstraete et al., 2009, Miller, 2006, World Health Organisation (WHO), 2015). Freshwater scarcity can cause an overexploitation of conventional water resources, leading to unsustainable solutions and significant impacts for the environment. This scenario can compromise the social and industrial development, as well as the water bodies status (in terms of quantity and quality), so that it becomes of great importance to preserve freshwater and use it efficiently.

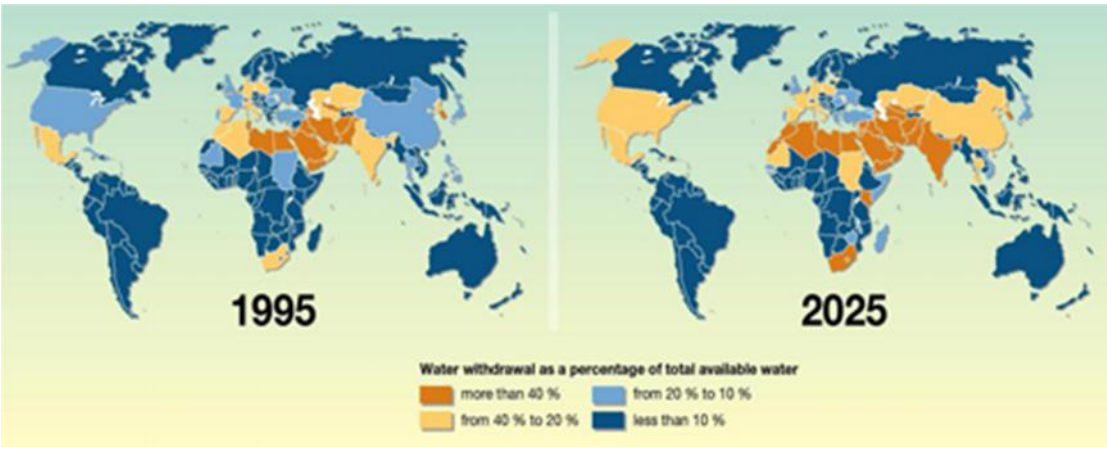

Figure 1.1. Water withdrawal as a percentage of total available water in 1995 and projected in 2025. Source: Rekacewicz, 2006.

Water treatment sector is directly affected by water scarcity and hence, it requires efficient operations and sustainable management of water resources. On one hand, water utilities have to construct/update existing treatment processes to deal with compromised water resources (both conventional and alternative) and maximise the processes water yield. Simultaneously, legal requirements in terms of water quality delivered/discharged are becoming more stringent (Jacangelo et al., 1997a, Meier et al., 2006, Pressdee et al., 2006), so that water managers not only have to face more adverse water quality and quantity issues, but also provide more efficient solutions, in technical, economic and environmental terms. As a result, the implementation of more advanced and efficient technologies is of utmost importance.

1.2. Drinking water treatment processes

Drinking water treatment plants (DWTPs) aim at providing safe drinking water to the communities they serve in a reliable way (US EPA, 2009). Depending on the characteristics of each system and the quality and origin of the water resource, different unitary processes are applied to fulfil the product water sanitary requirements. In 1975 the European Commission (EC) approved the Directive 75/440/EEC, which defined the necessary treatment train based on the quality of the surface water abstracted for potabilisation purposes. Currently, the Drinking Water Directive 98/83/EEC establishes the required quality of water intended for human consumption at European level, and it was transposed into Spanish law by the Royal Decree 140/2003. The treatment train that should be implemented in each case, based on the feed water quality, is not defined in the present directive. In 2014 the EC conducted a public consultation on the European Union (EU) quality of drinking water to identify the needs for improvement of the current legislation. In April 2015 the Drinking Water Committee agreed on adapting the current 98/83/EEC annexes to scientific and technical progress. It is expected to be adopted during 2015, if there are no objections from the Council and the Parliament, and to enter into application in 2017 (European Commission, 2015). The approach of the update is that the DWTPs become proactive rather than reactive, following the hazard analysis and critical control point (HACCP) principle from the food regulation and the water safety plans (WSP) described in the Guidelines for Drinking Water Quality from the World Health Organisation (WHO). This will enable a better management and problem oriented monitoring, reducing the unnecessary analyses and focusing on the more meaningful ones.

The water scarcity context together with the sanitary and environmental protection needs pose some upcoming challenges for the DWTPs:

- To present high elimination yields of microbiological and chemical contaminants, especially those considered emerging and priority. Additionally, technologies that minimise disinfection by-products (DBP) formation should be explored
- To minimise water losses
- To present the capacity to treat low quality water resources

- To minimise the generated wastes during drinking production and convert them into a new resources with added value
- To present low energy consumption, by using renewable energies, heats or residual products, or offering a greater energetic efficiency
- To provoke an equal or lower environmental impact than conventional technologies
- To be integrated in preventive water quality systems (e.g. WSP), enabling the optimisation of the quality control costs, improving the quality and minimising its associated risks

1.2.1. DWTP conventional pre-treatment

Different unitary processes may compose a DWTP, including aeration and air stripping, chemical oxidation, coagulation and flocculation, sedimentation and flotation, granular media filtration, membranes, ion exchange and adsorption of inorganic contaminants, chemical precipitation, adsorption of organic compounds, chemical disinfection and UV technologies (Edzwald, 2011). Among them, coagulation/flocculation, sedimentation and granular media filtration are typically considered as DWTPs pre-treatment units since their main function is to remove coarse solids and particles to protect the subsequent stages, and hence, enable a better functioning of the latter. This treatment scheme is the most widely implemented water treatment technology and has been used since the early 20th century (Safewater). Nevertheless, it has some limitations mainly related to chemical consumption, sludge production, water losses and space requirements.

i) Chemicals consumption

The Spanish Royal Decree 140/2003 regulates the use of disinfectant products, coagulants and flocculants for the treatment of drinking water. Polyacrylamide, a common polyelectrolyte added to the intake water in order to enhance coagulation, appeared among the permitted substances in the Decree. The Order SCO/317/2005 came into effect in 2005 as an update of the Royal Decree 140/2003. Among other implementations, the Order restricted the substances allowed in the water treatment and provided the minimum requirements for water monitoring. With regards to polyacrylamide, its use was allowed by the Order with restrictions (the average dosage could not exceed an average value of 0.02 mg/L) and an additional analytical control was required. On 17th July 2009, a new order was promulgated (Order SAS/1915/2009) as an update of the Order SCO/317/2005. This new Order is still more stringent than the previous one. Polyacrylamides, for example, are not included anymore in the list of allowed disinfectant products, coagulants and flocculants permitted for the treatment of drinking water. It is clear, thus, that new treatment strategies are necessary to meet the new regulations.

The average consumption of chemicals in pre-treatment steps of DWTPs is 0.03 kg/m^3 of raw river water (Adham et al., 2006). Therefore, a large DWTP collecting 300,000 m^3 of raw river

water/day would need 9,000 kg/day of coagulants and flocculants, representing a large chemical consumption.

ii) Sludge production

The increase in stringency of international and national water treatment requirements has led to a progressive increase of sludge produced. Babatunda and Zhaoa (2007) quantified in several million tons the annual production of waterworks sludge in Europe, estimating a two-fold increase by the next decade. As a result, for many EU Member States the sludge produced in water treatment facilities has turn into a major problem because its application in agriculture is limited and sometimes not feasible due to logistic issues: the greater production is found in big cities, leading to a high transport cost (with its associated emissions) which makes the process unfeasible in economic and sustainable terms (European Commission).

Conventional coagulation-flocculation pre-treatment generates large quantities of sludge. Cornwell (2006) reported the coagulant sludge flows to be between 0.1 – 3.0% (in volume) of the water treatment plant throughput and Verrelli (2008) reviewed surveys stating values from 0.1 to 4.5% (in volume) and up to 10% (in volume) or more of the plant capacity for filter backwash flows. Thus, it is evident that new pre-treatment strategies that could help reduce sludge generation need to be developed and adopted. In order to exemplify the importance of the environmental problem linked to the sludge generation, a DWTP using 300,000 m^3 of raw river water/day and generating 0.04 m^3 of sludge/m^3 of raw water would produce around 12,000 m^3 of sludge/day.

iii) Raw water losses

Water lost during the conventional pre-treatment can reach 15% of the inlet flow (data from various DWTPs), which turns into a non-used valuable resource, especially in semi-arid regions. In this context, drinking water treatment steps need to be optimised in terms of maximum valorisation of raw water (i.e. minimal water losses). Following the previous example, a DWTP collecting 300,000 m^3 of raw river water/day, would lose around 45,000 m^3 of raw river water/day due to raw water losses linked to its pre-treatment.

iv) Space limitations

The space available to install DWTP facilities is becoming more limited, especially in urban zones, due to the growth of cities and the necessity to enlarge the existing plants to fulfil the new requirements in terms of produced water quality. Therefore, future DWTP should be composed of technologies with reduced footprint in order to be integrated in the urban scheme. Conventional pre-treatment typically occupies 35-40 m^2/(1,000 m^3 permeate/day) (Wilf, 2004).

1.2.2. *Membrane based DWTPs pre-treatment*

i) Low pressure membrane technology

Membrane technology has significantly evolved in the last decades, becoming a technological solution increasingly applied in water treatment plants (Pressdee et al., 2006, Huang et al., 2009); particularly, low pressure membrane systems (microfiltration (MF) and ultrafiltration (UF)) within the drinking water treatment sector (Guo et al., 2010). Its global installed volume has raised at an impressive rate during the last 10 years (Figure 1.2). Forecasts predict a consistent growth of the installed capacity for the upcoming years, especially in the desalination and industrial segments, but not limited to them (Figure 1.2).

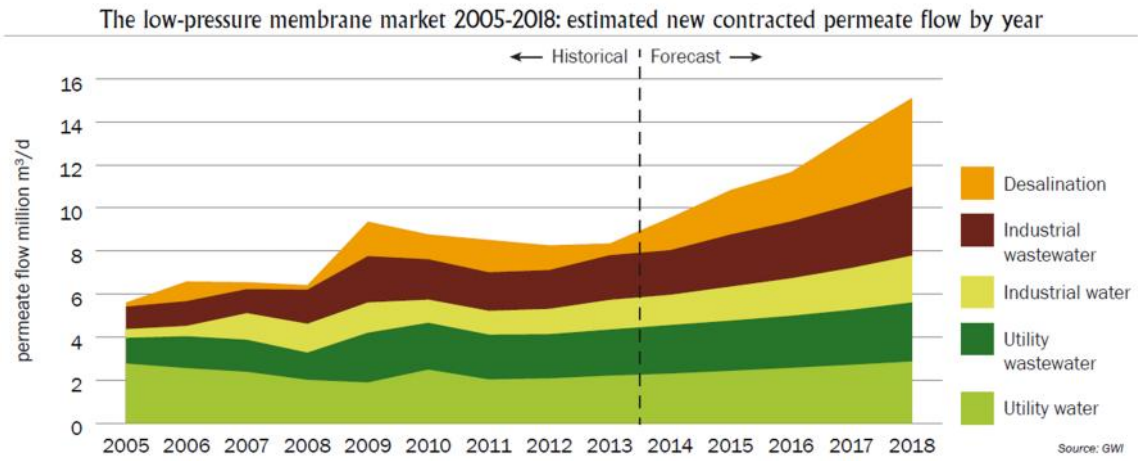

Figure 1.2. Low pressure membranes installed capacity evolution (2005 – 2018). Source: Global Water Intelligence, GWI (2014).

The wide implementation of low pressure membranes can be attributed to numerous factors such as increased stringency of water quality legislation that cannot be effectively fulfilled by conventional treatment processes, impoverishment of freshwater quality, increasing tendency of using alternative water resources such as brackish water or reclaimed wastewater, improved membranes performance, diminishment of their associated costs, operation and automation easiness, minimum staffing requirements, modularity, easy scaling-up, reduced space requirements, independence of water source quality and development of new applications for membrane processes (Guo et al., 2010, Jacangelo et al., 1997a, Meier et al., 2006, Mulder, 1996).

Low pressure membranes, whose molecular weight cut off is in the range of 10,000 to 500,000 Dalton, are able to produce high quality water independently of incoming water quality fluctuations. They present a high level of pathogen removal, such as viruses, bacteria and protozoa cysts (Giardia and Cryptosporidium) (Guo et al., 2010). Complete removal of coliform bacteria, Giardia spp. and Cryptosporidium spp. by MF and UF membranes has been demonstrated by many researchers (Adham and Jacangelo, 1994, Edwards et al., 2001, Freeman et al., 1996, Hirata and Hashimoto, 1998, Jacangelo et al., 1991). Compared to MF, UF

technology is able to remove some viruses thanks to its lower cut-off (Melin and Rautenbach, 2003) and hence, it can contribute to disinfect water, minimising the use of chemical disinfectants (Rojas et al., 2008), often related to DBPs formation. In addition to this, low pressure membranes have also been claimed to diminish the formation of DBPs by contributing to the overall removal of DBP precursor when combined with coagulation or adsorption.

Commonly, low pressure membrane systems within a water treatment facility are implemented in (Farahbakhsh et al., 2004):

- Existing conventional water treatment plants which may be composed of coagulation, flocculation, solid separation and filtration, where MF/UF substitutes sedimentation-filtration units.
- New water treatment processes aiming at reducing total organic carbon (TOC) and other substances of possible concern
- Water treatment plants where MF/UF are used together with other unitary processes such as nanofiltration (NF) or reverse osmosis (RO) where the former operate as pre-treatment of the latter

Low pressure membranes present different configurations: tubular, capillary, hollow fibre, flat sheet, etc. Hollow fibre is the most commonly used within the drinking water treatment field (EPA, 2001). They are typically made of organic polymers, such as polypropylene (PP), polyvinyl difluoride (PVDF), polysulfone (PS), polyethersulfone (PES) or cellulose acetate (CA). These materials present different characteristics, such as pH and oxidant sensitivity, surface charge and hydrophobicity, which determine their performance and operational constraints. Hollow fibre modules can be pressurised or submerged, depending if a positive pressure is applied before the membrane module, to push the fluid, or a vacuum pump is located after the membrane module, to suck the fluid. The pressurised modules can either present an inside-out or outside-in flow direction, whereas the submerged ones can only be outside-in. In the outside-in configuration, the feed water flows from the outside of the fibre to the lumen, being the retained particles and colloids collected on the outer of the fibre and the permeate in the interior channel of the fibre. In the case of the inside-out, the feed water enters the lumen of the fibre and the treated water is collected on the outside of the fibre, being the retained particles collected in the inside of the fibre.

Membrane modules can be operated in dead end or cross flow modes. The former involves all the feed water being filtered through the membrane, accumulating the retained particles and colloids into/onto the membrane surface until a backwash (BW) is conducted. In a cross flow pattern, the feed flow moves tangentially to the membrane, in order to limit the extent of particle deposition and foulants cake formation on the membrane surface. Therefore, this mode limits the fouling extent, but it requires the existence of a recirculation stream.

Fouling is considered as the main limiting factor for a wider implementation of membrane filtration processes (Huang et al., 2009). Because of the accumulation of organic colloids and other particles retained by low pressure membranes, the membrane porous structure is modified through different blocking laws: complete blocking, standard blocking, intermediate blocking and/or cake filtration (Hlavacek and Bouchet, 1993, Iritani, 2013). Complete and intermediate pore blocking are related to the sealing of pores entrances, standard blocking to pore constriction and cake filtration to the formation of a foulants layer external to the membrane (Iritani, 2013). Literature identifies pore blocking as the predominant mechanism of irreversible fouling (Neubrand et al., 2010), which cannot be removed by physical and/or chemical means, involving a large permeability loss (Iritani, 2013). Due to fouling, the membrane permeability is decreased and hence, to produce a given flux, greater transmembrane pressures (TMPs) are required. In addition to this, because the porous structure may be modified, the quality of the permeate produced could vary as well.

In order to minimise fouling effects, pre-treatments to low pressure membrane processes can be applied, such as coagulation, adsorption or pre-oxidation. Precoagulation (with or without sedimentation) has been defined as the most successful pre-treatment to reduce fouling on low pressure membranes (Huang et al., 2009). It has been hypothesised that a protective cake is formed, which prevents some compounds depositing into/onto the membrane (i.e. changing the main fouling mechanism) or lead to a more porous cake turning into to less resistance gain over the filtration cycle (Blankert et al., 2007). When combining precoagulation and UF, the conditions and doses applied are not the same as those used in conventional water treatment (Pearce, 2008, Fiksdal and Leiknes, 2006, Huang et al., 2009), being typically 40% or less (Pearce, 2008). Some works have identified the existence of an optimal dose, above/below which hydraulic detrimental effects occur on the subsequent UF (Wang et al., 2013). On the other hand, because dissolved organics pass through low pressure membranes, a precoagulation may also contribute to retain these substances which could otherwise foul subsequent NF/RO stages (Pearce, 2008). Indeed, certain contaminants, such as particles, microorganisms, humic substances, etc. can be embedded into the formed flocs and thus, be retained by the low pressure membrane (Lerch et al., 2005a) and not reach the NF/RO stage. The optimal coagulant dose targeting maximum dissolved organic carbon (DOC) removal may differ from that aiming at minimising membrane resistance increase during filtration. So based on the process treatment objectives, the optimum coagulant dose for a given water resource should be determined experimentally.

Even if fouling is minimised, cleaning strategies need to be applied to overcome its associated negative effects. Hydraulic cleaning, also referred as backwash, typically involves reversing the filtration flux, conducting an aeration and/or a flushing step, detaching those foulants not tightly bounded to the membrane, which encompass the so called physically reversible fouling. Aiming at removing those foulants with membrane affinity, chemicals are dosed during the cleaning operations, being those removed the chemically reversible foulants and those not dislodged the irreversible ones. The frequency of the cleaning operations will depend on the fouling nature and extent.

Besides decreasing the overall process water production and increasing the energy consumption (Tabatabai, 2014), a frequent membrane cleaning, especially when chemicals are dosed, can enhance membrane ageing (LeClech, 2014), which is another concern of membrane based processes (Jacangelo et al., 1997b). When membranes are compromised, both by physical or chemical means, their separation properties cannot be guaranteed. As a result, the monitoring of membrane integrity is of utmost importance for plant operators.

ii) Low pressure membranes as pre-treatment to high pressure membranes

As previously mentioned one of the applications of low pressure membranes is as pre-treatment to high pressure membranes (NF, RO) for seawater, brackish water and wastewater processing. The objective of a pre-treatment to a NF or RO membrane is to remove particles, reduce organics and provide a feed stream that will not cause fouling on the subsequent RO/NF elements (Pearce, 2008). As described earlier, conventional pre-treatment is based on chemical treatment and media filtration, often relying the latter on gravity-driven granular media filtration, which commonly presents nominal diameters in the range of 0.5 – 0.6 mm (EPA, 1995). UF/MF relies on the sieving effect offered by a porous structure, highly uniform and with a narrow pore size distribution (typical UF pore sizes: 0.1 – 0.01 μm). It represents a barrier to particles above the size of the membrane pores, and thus, produces a higher quality feed water to the subsequent NF/RO. This leads to less fouling, reduced chemical usage and better on-stream time, reducing the overall treatment costs and improving the security of supply (Pearce, 2008). As a result, membrane based processes, and in particular UF has gradually gained acceptance as the preferred pre-treatment to RO (Pearce, 2008).

A comparison of conventional pre-treatment and UF/MF based pre-treatment to RO units are listed in Table 1.1, highlighting the advantages of the membrane based treatment scheme per category. Briefly, they can be summarised as (Fritzmann et al., 2007, Pearce, 2007):

- Greater capacity of treating surface water with poor and/or variable quality
- Increased reliance of pre-treated water quality: avoidance of operation out of RO feed specifications
- Higher RO design flux and recovery, turning into lower capital costs
- Less fouling occurrence in the subsequent RO system
- Increased RO lifetime, leading to significantly reduced RO membrane replacement
- lower space requirements: up to 30 - 50% of savings when using UF
- lower (or nil) chemical dosage in the pre-treatment stage, encompassing lower waste generation and avoiding special safety measures and careful harmonisation and control of water chemistry in view of the requirements of downstream treatment steps

- Reduced requirement for RO disinfection and cleaning (i.e. decreased system downtime, water losses and chemicals dosed)

Table 1.1. Comparison of conventional and UF pre-treatments to RO. SDI: silt density index. Source: Adapted from Pearce (2007), Fritzmann et al. (2007).

	Conventional pre-treatment	UF pre-treatment	Benefits
Capital costs	Cost competitive with UF	Slightly higher than conventional pre-treatment. Costs continue to decline as developments are made	Capital costs of UF could be 0 – 25% higher, whereas life cycle costs using either of the treatment schemes are comparable
Footprint	Calls for larger footprint	Significant smaller footprint	Footprint of UF could be 30-50% of conventional size
Energy requirements	Less than UF as it could be gravity flow	Higher than conventional	UF requires water pumping through the membranes
Chemical costs	High due to coagulant and process chemicals needed for optimisation and operation	Chemicals use is low, dependent on raw water quality	Less chemicals needed in UF pre-treatment
RO capital costs	Higher than UF since RO operates at lower flux	Higher flux is logically possible resulting in lower capital cost	Due to lower SDI values, RO could be operated at 20% higher flux if feasible, reducing RO capital costs
RO operating costs	Higher costs as fouling potential of RO feed water is high resulting in higher operating pressure. Frequent cleaning of RO membranes needed	Lower RO operating costs are expected due to lower fouling potential and longer membrane lifetime	The net driving pressure is likely to be lower if the feed water is pre-treated by UF. Membrane cleaning frequency could be reduced by 10-100%,reducing the system downtime and prolonging element lifetime

The cost savings on operation can be expected to be significant. Table 1.2 compares the general costs (Table 1.2 top) and the chemical operating cost (Table 1.2 bottom) associated with conventional and MF/UF pre-treatment options. As can be seen, capital expenditures are 3% higher for the direct UF/MF scheme. Nevertheless, in the case of the cleaning operational expenditures, it becomes more economic than conventional pre-treatment. Pearce (2007) estimated a cleaning frequency of the subsequent RO unit of three times a year when water was pre-treated conventionally, whereas once or twice when direct UF/MF was in place. This corresponded to savings of 45% and 64% approximately by the adoption of direct UF/MF as RO pre-treatment.

Table 1.2. Comparison of the general costs (top) and the chemical operating cost (bottom) associated with both different pre-treatment options. DMF: dual media filter, (*) based on amortization capital at 8% over 20 years. Source: Pearce (2007).

Pre-treatment process	Conventional	UF/MF
Capital expenditure	k$	k$
RO and racks	2,000	2,000
Pre-treatment (DMF's/racks)	800	1700
Process equipment, pumps, site works	14,050	13,850
Indirect	5,900	5,900
Total	22,750	23,450
Amortization(*), k$/y	2,284	2,354

Pre-treatment process	Conventional	UF/MF	UF/MF
RO cleans/y	3	2	1
Operating costs - chemicals	k$	k$	k$
Dosing and UF/MF cleaning	61.4	24.1	24.1
RO cleaning	83.5	55.7	27.8
Total	144.9	79.8	51.9

However, MF/UF are still considered an expensive option, and consequently their application is often restricted to very specific situations (Pearce, 2008). For example, in wastewater treatment UF/MF is the pre-treatment technology selected due to the highly fouling nature of the feed (Pearce, 2008).

iii) Direct UF as an alternative to conventional pre-treatment in DWTP

As described, low pressure membranes are mostly implemented as a part of the pre-treatment of conventional processes, for instance substituting sand filtration, or as a pre-treatment of high pressure membranes in seawater, brackish water or wastewater treatment schemes. Nevertheless, the option of substituting the pre-treatment (totally or partially) and simultaneously delivering water to a high pressure membrane system can be explored, especially for surface water. Direct UF consists in treating raw river water directly by UF without any preliminary unitary process. This could provide the benefits of high quality consistently being produced, with its positive impacts on the subsequent RO discussed earlier, a reduction of chemical dosage to the feed water, together with a compact system, avoiding the operation of complex multi-stage processes which impact one to another. Nevertheless, some challenges may arise, because the implementation of UF has typically been either with feed water of stable quality (e.g. seawater) or with pre-treated water (e.g. after coagulation/flocculation, settling, sand filtration).

An extensive review of previous direct UF projects conducted worldwide was undertaken. The scarce experiences found were conducted with surface water (canals, reservoirs, springs and rivers) and reported different results. Li and Dong (2008) concluded that direct UF was not suitable to treat raw river water without any pre-treatment because the TMP increased quickly and the membrane became seriously fouled after 6h of operation. Other works faced technical difficulties when implementing direct UF, especially during high turbidity events. Clever et al. (2000) assessed direct UF of river water (of unknown turbidity) by means of a dead end module (35 m^2) for 10 months and reported some problems during high turbidity events when temperatures were below 10 ºC. Pianta et al. (1998) worked with karstic spring water (presenting mean turbidity of 1.5 NTU but up to 130 NTU during storm events) both in dead end and cross flow modes (7.2 m^2 UF membrane surface area) for 12 months. It was concluded that direct UF (dead end mode) working at 140 L/(m^2·h) was appropriate for karstic waters with turbidity peaks below 20 NTU and for a short period of time; under greater turbidity scenarios, cross flow should be applied (70 L/(m^2·h) could be maintained during 5 consecutive days at mean turbidity of 40 NTU). On the other hand, other studies reported successful results, confirming the feasibility of UF as an alternative to coagulation, sedimentation/flotation and rapid sand filtration (Oosterom et al., 1998), being feasible especially for those waters with high variability in quality (Rojas et al., 2008). For example, Rojas et al. (2008) worked with reservoir water (4 - 13 NTU) during 180 days at 54 L/(m^2·h) of filtration flux and 93% of water yield (ratio between net permeate produced and intaken water), Hofman et al. (1998) with canal water (12 – 40 NTU) for almost 1 year, at filtration fluxes of 70 – 100 L/(m^2·h), Xia et al. (2004b) with reservoir water (average turbidity 23 NTU) during an unreported period of time and under unknown filtration conditions, Vos et al. (1998) with canal water (20 - 70 NTU) for 11 - 30 days at 50 L/(m^2·h), only achievable after optimising the backwash and chemical cleaning operations, and Oosterom et al. (1998) with surface water of unreported quality, during 800 h, experimenting a large decrease in permeability (from > 400 L/(m^2·h·bar) to < 50 L/(m^2·h·bar)) after 200 h of filtration. Moreover, the reported water yields for UF of surface water without extensive pre-treatment were generally low; Schlichter et al. (2004) quantified them in 70 - 90%.

As can be seen, the previously described works were performed with low turbidity surface water and most of them for a limited period of time. These experimental limitations, together with the discrepancy of the conclusions drawn regarding the technical feasibility of direct UF, highlight the need of further research. In addition to this, some authors stated that more investigation was needed to optimise the membranes performance on the direct treatment of surface water (Oosterom et al., 1998).

As commented, fouling is considered the main limiting factor for a wider membrane filtration processes implementation (Huang et al., 2009, Park et al., 2002). Within the direct UF framework, fouling may even be a greater challenge since no previous unitary process partially removing it is considered. Indeed, Lerch et al. (2005a) stated that direct treatment of surface water by UF was not implemented yet at large scale due to fouling and scaling. As a result, various experiences reported contrasted direct UF without and with pre-treatments,

comparing the addition of different coagulants (chitosan and aluminium and iron based salts) (Bergamasco et al., 2011, Chen et al., 2007, Guigui et al., 2012, Konieczny et al., 2006, Konieczny et al., 2009, Neubrand et al., 2010, Park et al., 2002, Wang and Wang, 2006, Xia et al. 2004a, Xia et al., 2007a, Xiangli et al., 2008), adsorbents (powdered activated carbon (PAC)) (Mozia and Tomaszewska, 2004, Pianta et al., 1998, Xia et al., 2007b, Yuasa, 1998) and/or oxidants (ozone and permanganate) (Heng et al., 2007, Karnik et al., 2005, Schlichter et al., 2004, Vos et al., 1998) to enhance the direct UF performance.

According to the available literature, coagulation – UF presented a lower flux decline than direct UF (Bergamasco et al., 2011, Chen et al., 2007, Guigui et al., 2012, Lerch et al., 2005a, Neubrand et al., 2010, Park et al., 2002, Wang and Wang, 2006, Xia et al., 2007a, Xiangli et al., 2008) and several works noticed an alleviation of fouling on the UF membrane due to the previous coagulation (Neudrand et al., 2010, Xia et al., 2007a, Wang and Wang, 2006).
Despite ultrafiltered water already presented a high quality (Clever et al., 2000, Hofman et al., 1998, Rojas et al., 2008, Xia et al., 2004b) when a previous coagulation was in place its quality could be enhanced, especially in terms of organic matter content (commonly quantified by DOC and UV_{254}) (Bergamasco et al., 2011, Chen et al., 2007, Guigui et al., 2012, Konieczny et al., 2006, Konieczny et al., 2009, Park et al., 2002, Xia et al., 2004a, Xia et al., 2007a, Wang and Wang, 2006). Park et al. (2002) related the higher removal of organic matter with the improvement of membrane filterability when a previous coagulation was in place, hypothesizing that the removed compounds contributed to the decrease in the UF membrane permeability. However, within the same study, larger UV_{254} removals were quantified simultaneously to higher permeability decays, which did not support the hypothesis under those conditions. Doses applied varied from work to work (1 - 20 mg/L generally) and were often based on maximising the retention of organic matter rather than on the appropriateness of the generated flocs physical characteristics (e.g. size), arguing that flocs may be destructed when entering the membrane fibres (Lerch et al., 2005a). Coagulants normally dosed were inorganic salts, such as ferric chloride, ferric sulphate and polyaluminium chloride (PACl), and conclusions on their relative efficiency differed. Similarly to direct UF studies encountered in the literature, those focusing on coupling coagulation-UF for raw surface water treatment mainly considered low turbidity sources (< 40 NTU) (Xiangli et al., 2008) and the scale of the experiments was often laboratory (Chen et al., 2007, Konieczny et al., 2006, Konieczny et al., 2009, Park et al., 2002, Xia et al., 2004a, Wang and Wang, 2006) although pilot scale works could also be found (Xia et al., 2007b, Xiangli et al., 2008).

As mentioned above, PAC was also tested as an enhancer of direct UF performance (Mozia and Tomaszewska, 2004, Pianta et al., 1998, Xia et al., 2007b, Yuasa, 1998). According to the literature, two effects were envisaged: an increase in natural organic matter (NOM) removal, particularly low molecular weight organics which cannot be removed by UF alone (Mozia and Tomaszewska, 2004), and a modification of the foulants cake structure deposited onto the membrane (Pianta et al., 1998). The membrane acted like a physical barrier for PAC. The organic compounds were adsorbed on the PAC, not reaching the membrane (Xia et al., 2007b) and PAC particles, hard and aggressive, modified the fouling cake structure, probably

becoming more porous and easily backwashable (Pianta et al., 1998). Mozia and Tomaszewska (2004) quantified an increase from 42% to 55% of TOC removal when coupling PAC (100 mg/L) to UF compared to (direct) UF alone. Nevertheless, no improvement in terms of flux decline or backwash efficiency was experimented. Xia et al. (2007b) neither noticed differences in permeability loss with different PAC dosages (10, 20, 30 mg/L). Pianta et al. (1998) stated that PAC dosage (15 mg/L) led to a more stable UF operation, enabling the implementation of a higher filtration flux (90 L/(m^2·h) under cross flow mode) during high turbidity peaks in the raw water. The authors also noted that at lower PAC dosages (5 - 8 mg/L) permeability drop was similar to the experiments conducted without PAC dosage, but permeability recovery was faster at higher PAC dosages.

Ozone and permanganate were also added prior to UF in order to enhance UF membrane performance (Heng et al., 2007, Karnik et al., 2005, Schlichter et al., 2004, Vos et al., 1998). Karnik et al. (2005) reported a significant improvement in permeate quality in terms of BDPs formation when dosing ozone (1.5, 2.5 and 10 mg $O_{3(g)}$/L) prior to UF when dealing with lake water. Schlichter et al. (2004) found out that when the residual ozone concentration in the permeate was around 0.05 mg/L, stable and higher filtration fluxes were attainable, even suppressing the need to conduct backwashes. Heng et al. (2007), who combined permanganate and chlorine dosage prior to the UF for algae fouling control of reservoir water, achieved higher and stable specific flux and improved permeate quality compared to direct UF. Vos et al. (1998) experienced 50% increase in the subsequent membrane filtration flux when a 2.5 mg $KMnO_4$/L dosage was conducted, as well as a reduction of manganese content in UF permeate.

Table 1.3 summarises the case studies reported at the initial stage of this PhD where direct UF was assessed, being the first five focused on direct UF and the rest on the coupling of coagulation with direct UF. It is important to remark that the objective of some of the reviewed works was not the assessment of direct UF feasibility but the evaluation of the effect of coagulants on NOM removal, turbidity and fouling. Nevertheless, when experimental results of direct UF (without coagulation) were included in those studies to compare the effect of coagulants, they are reported in Table 1.3. Otherwise, when direct UF without coagulation was not considered (Liang et al., 2008, Qin et al., 2006, Xiao et al. 2012, Panglish et al., 2005, Sun et al., 2009) or when the focus of the work was the hybridisation of coagulation-UF, PAC-UF or oxidation-UF without considering the application of direct UF, they were not included. Some studies regarding MF coupled to coagulation or PAC addition, and direct NF were found (Leiknes et al., 2004, Lerch et al., 2005b, Lebeau et al., 1998, Futselaar et al. 2002, Futselaar et al., 2003) but because the core of this thesis was direct UF, they were not listed either in Table 1.3.

From the existing literature it could be concluded that the application of direct UF to treat surface water was proved, but at conditions fairly different from the ones proposed in this thesis (reduced period of time, relatively stable feed water quality, etc.). Therefore, this thesis

aimed at going a step forward and implementing direct UF in more challenging conditions: pilot scale, during 2 years and with highly variable incoming feed water, particularly in terms of high turbidity variations and hence, complementing existing scientific knowledge. Besides being of interest for the scientific community, this approach should provide results applicable for plant operators, engineering consultants and membrane manufacturers. Not only the technical feasibility of direct UF, its optimisation and its comparison with the current conventional pre-treatment was conducted, but also its reliability in terms of membrane integrity was addressed by defining and executing microbes based tailored tests, comparing different microorganisms to determine the most convenient ones.

Finally, additional benefits associated to direct UF were addressed from a complete treatment train perspective. Within the envisaged scheme, the subsequent unit after the direct UF one would be the RO racks. RO implementation has increased exponentially during the last decades due to its high rejection capacity (it retains nearly all colloidal and dissolved matter (Fitzmann et al., 2007)) and its significant decrease in terms of energy requirements (Elimelech and Philip, 2011). Nowadays, one of the main challenges related to thin film composite (TFC) RO membranes is its integrity (Misdan et al., 2012), because they are highly sensitive to certain chemicals, such as free chlorine, which affect their performance. Because the direct UF scheme was expected to avoid the need to dioxichlorinate raw river water and to decrease or even eliminate the dosage of coagulants, it could encompass additional advantages besides those related to a higher UF permeate quality. As a result, changes in physico-chemical and transport properties of RO membranes exposed to various chemicals currently dosed in the conventional pre-treatment were studied to complete this thesis.

Table 1.3.Main characteristics of direct UF case studies reported in the literature. HRT: hydraulic retention time. N.A. non applicable

Reference – (water source) Raw water characteristics	Coagulation type	Coagulant (dose)	Permeate characteristics	Filtration, backwashing & chemical cleaning conditions
Clever et al. (2000) - (surface) Turbidity: > 100 NTU; TOC: 4.2 mg/L	N.A.	No	Turbidity < 0.05 NTU; TOC: 3.5 mg/L	(dead end) Filtration flux: 40 – 70 L/(m^2·h); BW frequency: 15 min (cross flow) Filtration flux: 60 – 80 L/(m^2·h); BW frequency: 45 min, with <10 ppm NaClO
Hofman et al. (1998) - (canal) Turbidity: 12–40 NTU	N.A.	No	Turbidity < 0.1 NTU	BW frequency: 20 min, duration 30 s CEB: 3h (H_2O_2 [200 mg/L] + hydrochloric acid [pH: 1.5]), soaking duration: 20 min
Li and Dong (2008) - (surface & synthetic) Turbidity: 34.3 – 40.1 NTU; DOC: 1.51 - 4.00 mg/L; UV_{254}: 0.030-0.196 cm^{-1}	N.A.	No	Turbidity: 1.37 NTU; UV_{254} removal: 3.48%	No BW
Rojas et al. (2008) - (reservoir) Turbidity: 3.9 – 12.8 NTU; UV_{254}: 0.009 – 0.039 (dimensionless)	N.A.	No	Turbidity: 0.07 – 0.95 NTU; UV_{254}: 0.006 – 0.021 (dimensionless)	Filtration flux: 54 L/(m^2·h); Continuous aeration BW frequency: 60 min, duration 2 min Daily chemical cleaning with chlorine (100 mg/L); once a week with citric acid (pH: 4.5)
Xia et al. (2004b) - (reservoir) Turbidity: 23 NTU	N.A.	No	Turbidity < 0.2 NTU	Unreported
Bergamasco et al. (2011) - (river) Turbidity: 240 NTU; UV_{254}: 0.923 cm^{-1}	N.A.	No	Turbidity:99.6 – 99.7%; UV_{254}: 92.9 -96.0%	No BW
	Coagulation tank	Chitosan (1 mg/L)	Turbidity: 99.9%; UV_{254}: 91.8% - 99.4%	
		Aluminium sulphate (15 mg/L)	Turbidity: 99.8%; UV_{254}: 96.3% - 88.5%	
Chen et al. (2007) - (river) Turbidity: 5.3 - 37.6 NTU; DOC: 5.34 - 6.29 mg/L	N.A.	No	NOM: 8% removal	Unreported
	Coagulation tank (HRT 30 min) + settling (30 min)	Alum (10 mg/L)	NOM: 20.5%	BW frequency: 60 min, duration 70 s
Guigui et al. (2012) - (canal) Turbidity: 21 NTU; DOC: 3.9 mg/L; UV_{254}: 0.072 cm^{-1}	N.A.	No	NOM: 10% approx. removal	Filtration flux: 120 L/(m^2·h)
	In-line	$FeCl_3$, $FeSO_4$, PACl (dose: 0, 5, 20 mg/L)	NOM: 15-50% approx., depending on coagulant dose	
	In-line	$FeCl_3$ (6 mg/L)		

Konieczny et al. (2006) - (river) Turbidity: 10.17-11.12 NTU; UV_{254}: 0.100-0.131cm^{-1}	N.A.	No	Turbidity: 1.41 NTU; UV_{254}:0.067 cm^{-1}	Filtration flux: 20.5 L/(m^2·h) Backpulses frequency: every 10 min
	Coag tank + Settling	$FeCl_3$ (15 mg/L)	Turbidity: 0.88 NTU; UV_{254}:0.033 cm^{-1}	
	Coag tank + Settling	$Fe_2(SO_4)_3$ (15 mg/L)	Turbidity: 0.99 NTU; UV_{254}:0.031 cm^{-1}	
Konieczny et al. (2009) - (river) Turbidity: 15 NTU; TOC: 6.53 mg/L; UV_{254}: 0.175 cm^{-1}	N.A.	No	Turbidity: 3 NTU; TOC: 2.93 mg/L; UV_{254}: 0.116 cm^{-1}	Unreported
Turbidity: 13 FTU; TOC: 7.75 mg/L; UV_{254}: 0.195 cm^{-1}	In-line	$Al_2(SO_4)_3$ (2.9 mg/L)	Turbidity: 0 FTU; TOC: 2.42 mg/L; UV_{254}: 0.075 cm^{-1}	
Turbidity: 19 NTU; TOC: 9.36 mg/L; UV_{254}: 0.296 cm^{-1}		$Fe_2(SO_4)_3$ (3.0 mg/L)	Turbidity: 2 NTU; TOC: 3.83 mg/L; UV_{254}: 0.130 cm^{-1}	
Turbidity: 17 NTU; TOC: 7.40 mg/L; UV_{254}: 0.260 cm^{-1}		$FeCl_3$ (2.4 mg/L)	Turbidity: 2 NTU; TOC: 4.13 mg/L; UV_{254}: 0.135 cm^{-1}	
Neubrand et al. (2010) - (river) DOC: 6.8 – 7.8mg/L	N.A.	No	Unreported	Filtration flux: 70 L/(m^2·h) BW frequency: 30 min (250 L/(m^2·h)
	In-line	$FeClSO_4$ (2-4 mg/L)		
		PACl (2 – 4 mg/L)		
Park. et al. (2002) - (river) Turbidity: 2 - 5 NTU; DOC: 2.3 - 2.9 mg/L; UV_{254}: 0.029 – 0.036 cm^{-1}	N.A.	No	Unreported	Unreported
	Coagulation tank (HRT 12- 60 min) & in-line	PACl (4.1 mg/L as Al_2O_3)	UV_{254}: 34.3 – 36.3% removal	BW frequency: 20 min, duration 20 s (dead-end)
Wang and Wang (2006) - (synthetic) DOC: 5 mg/L; UV_{254}: 0.09 cm^{-1}	N.A.	No	DOC: 28%; UV_{254}: 40% removal	Unreported
	In-line (HRT 1 min)	$Al_2(SO_4)_3{\cdot}18H_2O$ (3.5 mg/L Al^{+3})	DOC: 53%; UV_{254}: 78%	
Xia et al. (2004a) - (reservoir) Turbidity: 23 NTU; TOC: 5.7 mg/L	N.A.	No	Turbidity: 0.1 NTU; TOC: 4.3 mg/L	Filtration flux: 190 L/(m^2·h) BW frequency: 30-80 min, duration 45s
	Coagulation tank	PACl (1 – 5 mg/L)	Turbidity: 0.1 NTU; TOC: 3.3 mg/L	
Xia et al. (2007a) - (river) Turbidity: 23 NTU; UV_{254}: 0.154 cm^{-1}; DOC: 5 mg/L	N.A.	No	DOC: 8.5%; UV_{254}: 10% removal	No BW
	In-line (mixer)	Alum (8 mg/L)	DOC: 39.5%; UV_{254}: 50%	
		Alum (14 mg/L)	DOC: 44.5%; UV_{254}: 65%	
Xiangli et al. (2008) - (river) Turbidity: 10 – 150 NTU	N.A.	No	Turbidity < 0.01 NTU	Filtration flux: 100 L/(m^2·h) Flushing (duration 10 s) + BW (duration 20s; 250 – 320 L/(m^2·h)) every 25 min

1.3. Case study: surface water with highly variable quality and flow

The lower stretch of the Llobregat River was selected as the case study of this thesis due to its particularities, representing a challenging scenario to test new treatment schemes. The Llobregat River is located in the north-east of Spain and provides water to Barcelona area, being one of the main resources. It receives water of 4,948 km^2, with an average rainfall ranging between <550 - 900 mm/year in its catchment and presents an average flow of 19 m^3/s (Hutzinger, 2012, Vegas-Vilarrúbia et al., 2012). Nonetheless, due to its Mediterranean behaviour, the rainfall pattern is irregular and presents extreme episodes, such as flash flood events, where its flow can be fifteen times greater than the average flow, or severe water scarcity episodes, like the one suffered in 2008, where the river flow was very low in the final river stretch (Hutzinger, 2012). Figure 1.3 plots the Llobregat River flow in Sant Joan Despí (SJD) DWTP intake during 2006 – 2010.

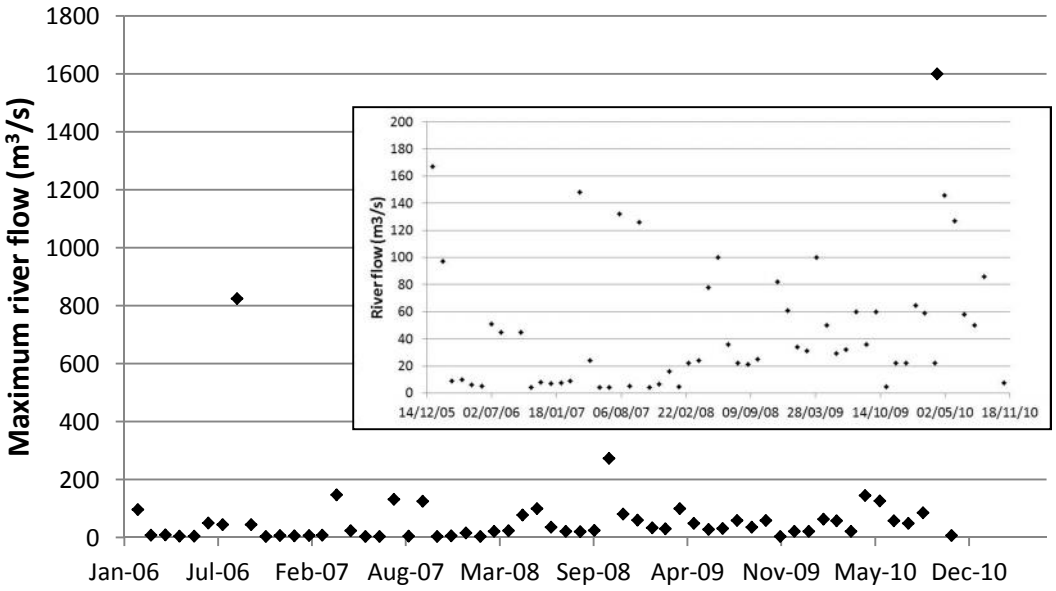

Figure 1.3. Llobregat River maximum flow in SJD DWTP intake during 2006 - 2010 in a monthly basis. A zoom between 0 – 200 m^3/s is depicted in order to show the river flow variability. Source: SJD DWTP, Aigües de Barcelona (AB).

The Llobregat River water quality has been strongly affected by industrial, urban and agricultural activities along the last century (Hutzinger, 2012). As a result, a wide range of pollutants, both macro-contaminants as well as micro-contaminants, can be found in this river (Farré, 2001, Kuster et al., 2008, López-Roldán, et al., 2010, Petrovic et al., 2002, Rodriguez-Mozaz et al., 2004a, Rodriguez-Mozaz et al., 2004b, Solé et al., 2000).

Turbidity, total organic carbon (TOC) and absorbance at 254 nm (UV_{254}) evolution along time are plotted in Figure 1.5, Figure 1.7 and Figure 1.8 respectively to illustrate the water quality variability of this river. Turbidity, which strongly affects MF/UF membranes (Mulder, 1996)

fluctuated from 1.0 to 39,000.0 NTU (average 262.9 NTU) during 2009-2014, whereas TOC from 0.10 to 17.00 mg/L (average 4.43 mg/L) and absorbance from below the limit of quantification to 0.4300 cm^{-1} (average 0.1167 cm^{-1}) for the same time period.

In Figure 1.6, the frequency of various turbidity episodes, classified into following turbidity ranges 0 – 50 NTU, 50 – 100 NTU, 100 – 150 NTU, 150 – 300 NTU, 300 – 500 NTU, 500 – 1,000 NTU and 1,000 – 39,000 NTU, is represented for the period January 2009 – November 2014. As can be seen, raw river water turbidity was below 150 NTU in 76.5% of the cases and below 300 NTU in 86.2% of occasions. The proportion of high turbidity episodes was quite significant, occurring during 5% of the time those above 1,000 NTU.

SJD DWTP is located in the lower part of the Llobregat River and supplies drinking water to almost 50% of the Barcelona Metropolitan Area, equivalent to 1.5 million inhabitants approximately. The SJD DWTP is a complex multistep treatment that combines a conventional pre-treatment, consisting on an oxidation with chlorine dioxide, coagulation/flocculation with aluminium salts, settling, sand filtration, followed by either ozonation and activated carbon filtration or by UF, RO and remineralisation, followed by a post chlorination (Figure 1.4). SJD DWTP conventional pre-treatment was compared to the performance of the direct UF prototype, since the latter was installed within SJD DWTP facilities and thus, both pre-treatments faced the same conditions simultaneously.

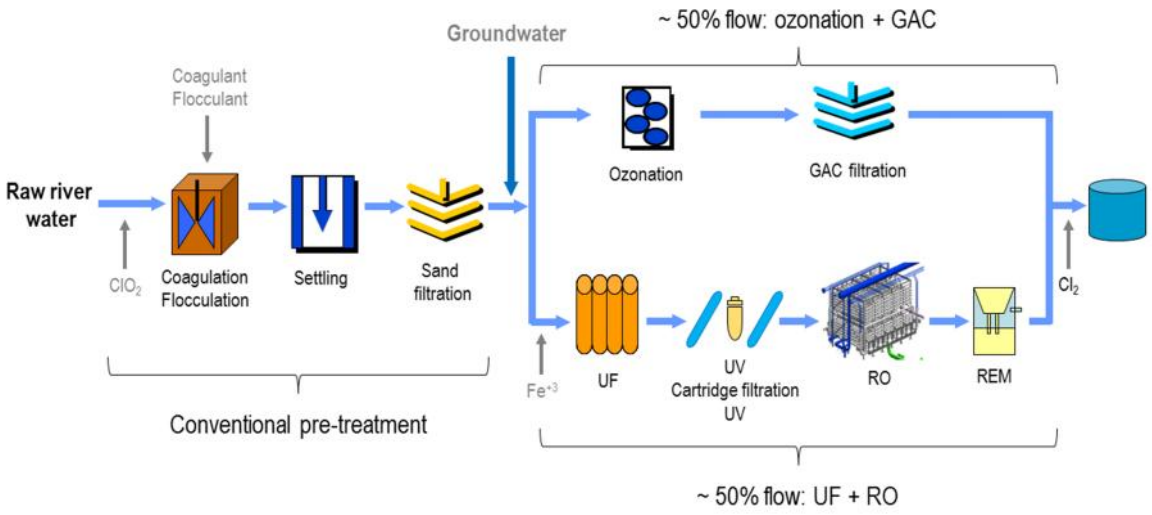

Figure 1.4. SJD DWTP current treatment scheme. GAC: granular activated carbon, REM: remineralisation.

The intake of Llobregat River by SJD DWTP is stopped when some water quality parameters from the raw river water surpass certain values in order to ensure that the process is not destabilised from an operational standpoint. These values are defined under normal conditions and under water scarcity conditions, when they are increased to maximise the water production. These values are included in Figure 1.5, Figure 1.7 and Figure 1.8 to illustrate when the conventional treatment would be stopped.

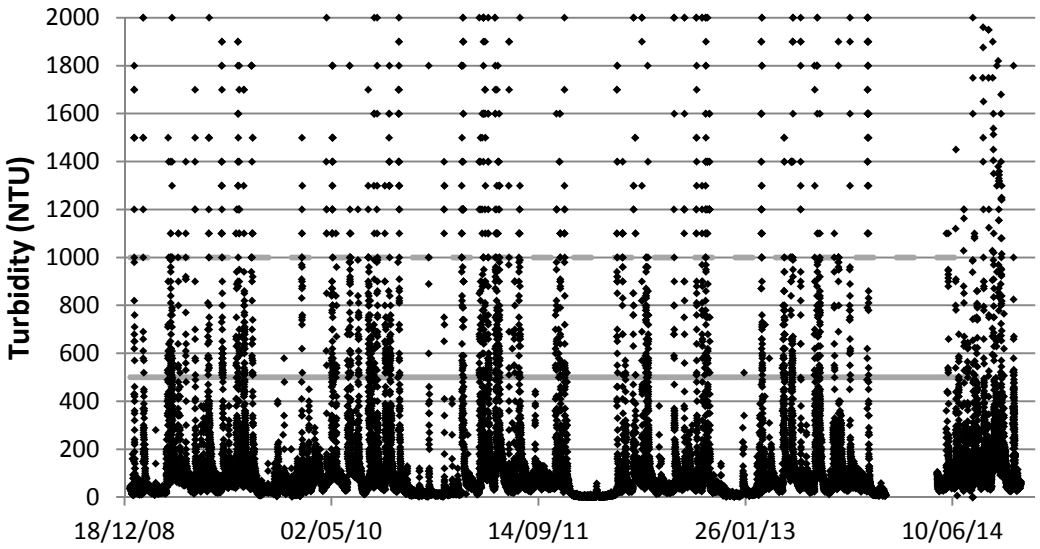

Figure 1.5. Raw river water turbidity evolution along time (January 2009 – November 2014) at SJD DWTP intake (black symbols). Above 450 NTU (solid grey line) and 1,000 NTU (dotted grey line) the SJD DWTP intake is stopped under normal and water scarcity conditions respectively. Source: SJD DWTP, AB.

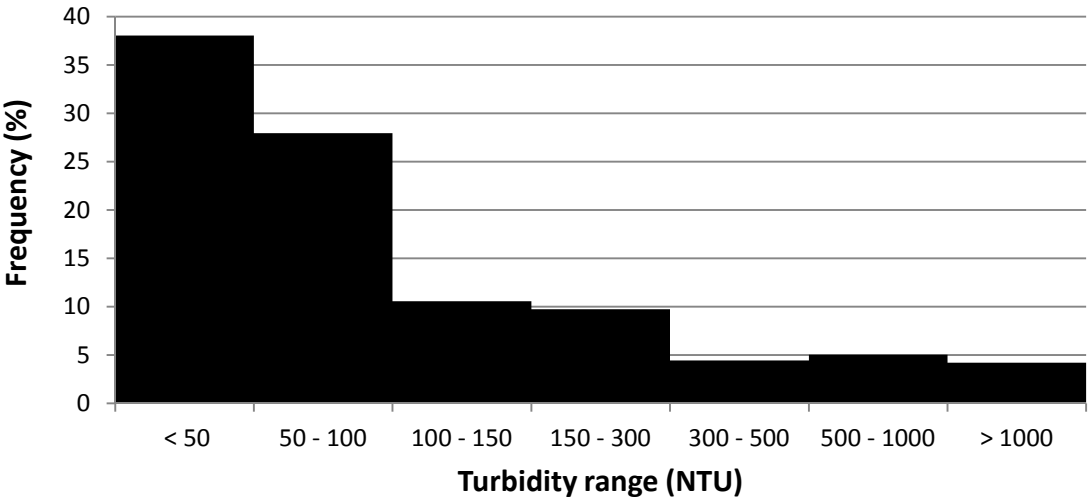

Figure 1.6. Histogram of raw river water turbidity from January 2009 to November 2014 at SJD DWTP intake. Source: SJD DWTP, AB.

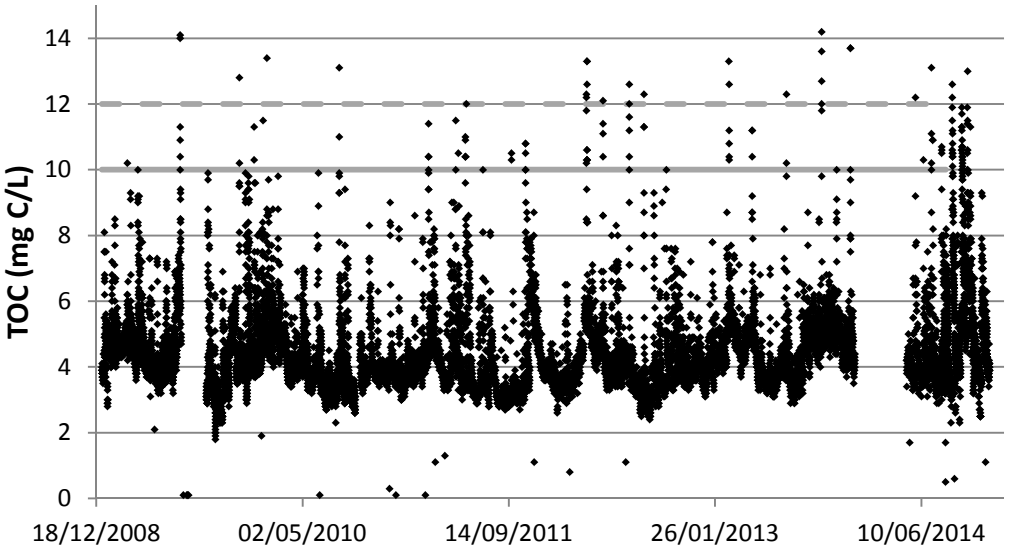

Figure 1.7. Raw river water TOC evolution along time (January 2009 – November 2014) at SJD DWTP intake. Above 10 mg C/L (solid grey line) and 12 mg C/L (dotted grey line) the SJD DWTP intake is stopped under normal and water scarcity conditions respectively. Source: SJD DWTP, AB.

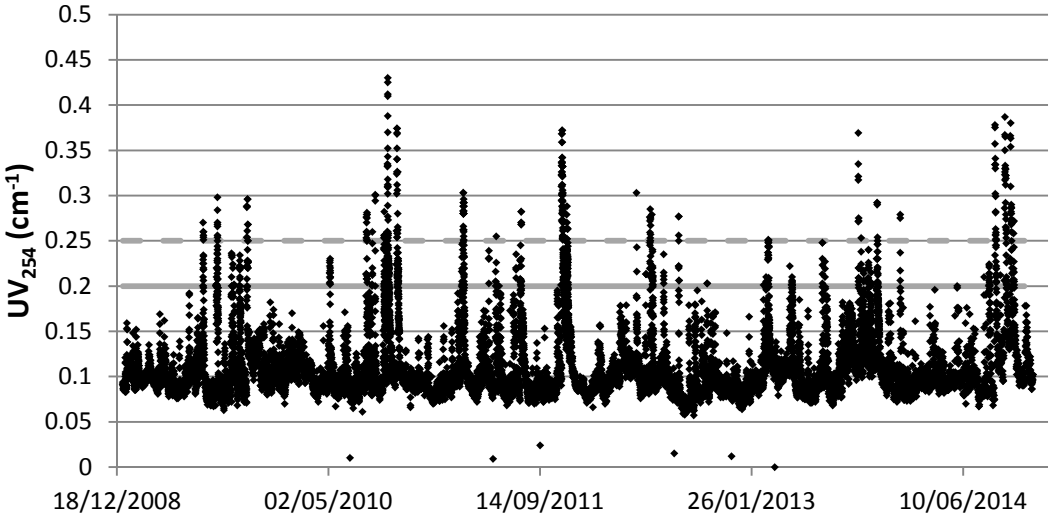

Figure 1.8. Raw river water UV_{254} evolution along time (January 2009 – November 2014) at SJD DWTP intake. Above 0.20 cm^{-1} (solid grey line) and 0.25 cm^{-1} (dotted grey line) the SJD DWTP intake is stopped under normal and water scarcity conditions respectively. Source: SJD DWTP, AB.

Figure 1.9, Figure 1.10 and Figure 1.11 correspond to the evolution along time of several microbiological parameters at the SJD DWTP intake. As can be seen, the total coliforms concentration ranged between 3 and 6 log_{10} units (MPN/100 mL), faecal coliforms between absence and 2 log_{10} units (MPN/100 mL) and aerobic bacteria at 37ºC between 4 and 6 log_{10} units (CFU/mL) approximately for the considered period.

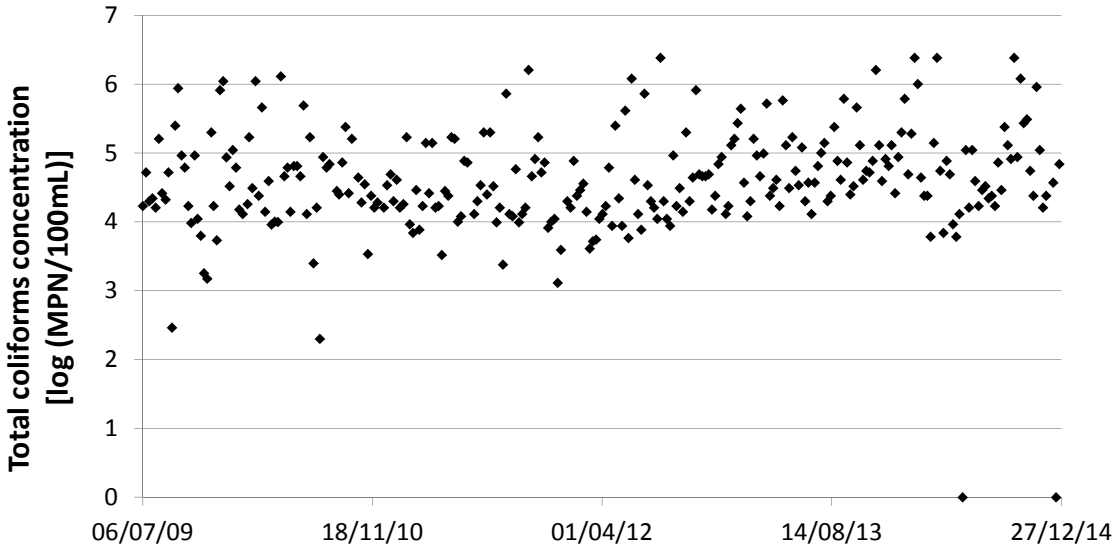

Figure 1.9. Raw river water total coliforms concentration evolution along time (July 2009 – December 2014) at SJD DWTP intake. MPN: most probable number. Source: SJD DWTP, AB.

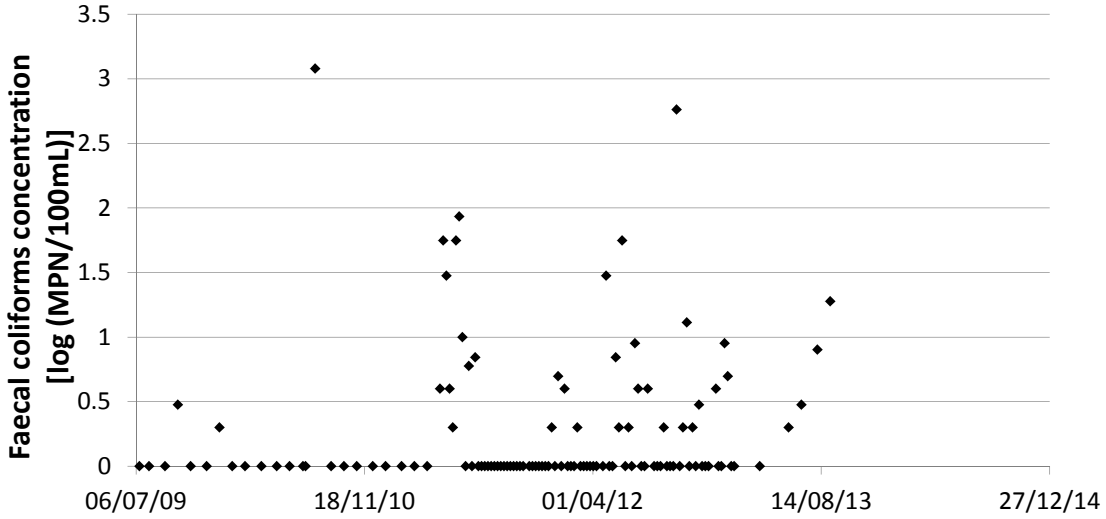

Figure 1.10. Raw river water faecal coliforms concentration evolution along time (July 2009 – December 2014) at SJD DWTP intake. Source: SJD DWTP, AB.

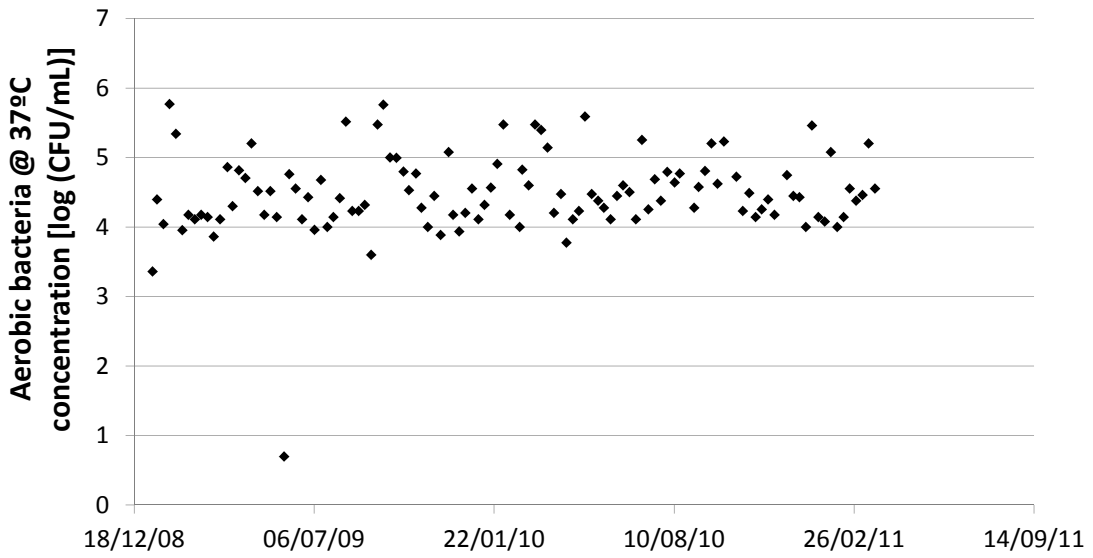

Figure 1.11. Raw river water total coliforms concentration evolution along time (January 2009 – September 2011) at SJD DWTP intake. CFU: colony forming unit. Source: SJD DWTP, AB.

Taking into account the high water quality variability of the Llobregat River at the SJD DWTP intake, assessing the feasibility of direct UF within this scenario was considered as appropriate: if it proved to be feasible in this case study, it would probably be applicable in several other sites presenting more stable conditions, since the technology was pushed into its limit the selected case study.

1.4. Objectives of this thesis

The preceding discussion led to the need for defining new treatment schemes for DWTPs, for validating their feasibility through studies whose results could be extrapolated to full scale systems and for optimising its performance. Taking into account the limitations of current conventional pre-treatment in DWTPs as well as the advantages that low pressure membrane systems show, the main research question this thesis aimed to answer was the capability of UF membranes to substitute conventional pre-treatment units (initial disinfection, coagulation / flocculation, settling and sand filtration) in DWTPs fed by highly variable surface water, by quantifying its advantages and limitations.

This was formulated as a proof of concept rather than as a specific assay on a given UF membrane or particular feed water source. For such purpose, several UF membranes were tested through this thesis with different properties, and, as commented before, a highly variable water source was studied to cover a wide range of scenarios, to ensure that the results could be extrapolated. Hollow fibre UF membranes were selected because it is the configuration more widely implemented in drinking water treatment (EPA, 2001) and presents two significant advantages. They are self-supported and strong enough to resist BWs, which make their operation easier especially in terms of fouling control, and present a high specific surface area, decreasing their associated investment costs. Among hollow fibre membranes,

the three existing configurations were addressed: a pressurised inside-out, a pressurised outside-in and a submerged outside-in systems, whose compositions were PES, PS and PVDF respectively.

As detailed previously, some initial studies addressing the substitution of conventional pre-treatment units by direct UF in DWTP were found in the literature, but most of them treating low turbidity feed water and/or for a limited period of time, reporting different results in terms of their feasibility. In addition to this, an optimisation of their operation under different scenarios, a detailed comparison with current conventional pre-treatment as well as a quantification of additional benefits in the subsequent treatment unit were lacking. Because real water long term studies at pilot scale are fundamental for membrane based processes, since fouling and ageing are two main issues determining their real implementation capacity, and because of the above-mentioned research gaps identified, the particular objectives of this thesis were:

- To evaluate at bench scale if UF (hollow fibre, pressurised outside-in, PS) could be an alternative to sand filtration in DWTPs treating highly variable surface water
- To assess at pilot scale if direct UF (hollow fibre, pressurised inside-out, PES) could substitute conventional pre-treatment (initial disinfection, coagulation / flocculation, settling and sand filtration) in DWTPs treating highly variable surface water, including extreme episodes (e.g. flash flood events) to identify the limits of the technology
- To optimise direct UF operation and to characterise the produced water quality (physico-chemically and microbiologically) under different scenarios aiming at comparing its performance with conventional pre-treatment and determining its competitiveness (removal capacity, variability, water yield, chemicals consumption,…)
- To elucidate membrane fouling reversibility of UF membranes depending on the cleaning operations characteristics
- To provide insights into the membrane fouling nature through the quantification of different fractions of natural organic matter (NOM) removal
- To define a protocol based on different microorganisms to determine the integrity of UF membranes, applicable to all the existing hollow fibre configurations, and to compare it to other integrity methods
- To determine membrane integrity of the direct UF scheme (hollow fibre, submerged outside-in, PVDF) along two years to provide insights into the long term feasibility of direct UF
- To elucidate additional benefits of direct UF on a subsequent RO stage in terms of RO membrane physico-chemical and transport properties

1.5. Methodology of this thesis

The nature of the experiments conducted within this thesis followed a progressive approach from conceptual and logistic perspectives. Initial bench scale tests aiming at evaluating the feasibility of a partial substitution of the conventional pre-treatment were followed by pilot scale experiments focusing on the complete substitution of the conventional pre-treatment. Finally, laboratory based assays were carried out to explore further impacts of direct UF on the subsequent unit (RO), complementing the study.

The bench scale system consisted of a UF outside-in PS hollow fibre module (Polymem UF0808M3 with a nominal pore size of 80 nm) operated under dead end filtration mode at constant TMP. It was fed by decanted water from SJD DWTP. Valves in the system were opened and closed manually to undertake the different operations (e.g. filtration, backwash). Permeate was collected for flux measurements and chemical analysis. TMP was measured by a pressure gauge.

The pilot scale system which was used to assess the direct UF hydraulic and quality performance was operated continuously during two years. It treated raw Llobregat River water, presented a nominal capacity of 5.0 m^3/h and worked under dead end filtration mode at constant permeate flow. It was equipped with a strainer to prevent excessive clogging of the subsequent inside-out pressurised hollow fibre UF (Pentair X-Flow Aquaflex - PES membranes with a nominal pore size of 20 nm), and was automatically controlled by a Scada system. The software enabled the modification of several variables, such as filtration time, permeate flow, cleaning conditions (frequency, duration, backwash flow, air flow, reagents nature and concentration), etc. so that the prototype was adaptable to the changing conditions. Cleaning operations were conducted automatically.

A second direct UF prototype, 15.0 m^3/h nominal capacity, was used for the membrane integrity tests. It worked in parallel to the abovementioned one and thus, it treated raw Llobregat river water during the same period of time. It consisted of a strainer, a coagulation tank with a stirrer and submerged outside-in PVDF membranes (1 membrane cassette with 10 Zenon Zeeweed® 500D modules of 40 nm pore size) contained in a 8,000 L feed tank. It was automatically controlled and several variables could be modified when needed. Cleaning operations were conducted automatically.

Hydraulic data from the bench scale system (filtration flow and TMP) was read manually in a frequency which sufficiently described the system behaviour. Hydraulic data from the prototype plants (feed flow, permeate flow, TMP, number of hydraulic cleanings (HCs) performed, number of chemically enhanced backwashes (CEBs) conducted,...) was recorded automatically by their central processing unit (CPU) and due to the high frequency data acquisition an excel macro was programmed, which ensured the meaningfulness of the records and helped its subsequent treatment. Some physico-chemical parameters, such as raw water turbidity, conductivity and temperature were recorded on line. Hydraulic resistance, which accounted for the membrane resistance itself and the resistance of the foulants

accumulated on the membrane, was calculated by Darcy's equation (Eq. 2.1). It was used to assess the membrane performance because it is temperature and filtration flux corrected, enabling the comparison between different schemes. Specific cake resistance was calculated (Eq. 4.3) as well in order to determine the increase of the cake layer resistance build up. Maintenance of the prototype and calibration of the sensing elements was conducted periodically.

The optimisation of the hydraulic conditions targeted the maximisation of the process water yield and the attainable fluxes. As a result, the conditions were progressively modified to assess the impact of each variable. In order to ensure that the hydraulic conditions set were bearable for the system, the prototype should be able to operate continually during several weeks without triggering the pre-set high resistance or TMP values.

The methodology used for the water quality analyses comprised a sampling protocol, which ensured the representativeness of the sample, and an analytical protocol, which was defined per parameter and was based on standard methods. The parameters monitored and the methods used were: temperature by resistivity (Endress & Hausser TR10-ABG1HD-SAG2000), conductivity by electrometry (Endress & Hausser CLS21D-C1+CM42-KAA000EAN00), pH by potenciometry (Hach-Lange DPD1P.99), turbidity by nephelometry (Hach-Lange Ultraturb SC at the prototype plant and Hach 21000 AN IS Turbidimeter at bench scale), total suspended solids (TSS) by ESS 340.2, absorbance at 254nm (UV_{254}) by spectrophotometry (Hach-Lange DR 5000), silt density index (SDI_{15}) and modified fouling index ($MFI_{0.45}$) by ASTM D4189 (Simple SDI Meter 9C-281-0157), DOC by combustion-infrared method using a DOC analyser (non purgeable organic carbon, UNE-EN 1484), after filtration with a 1.2 µm glass fibre filter for the raw water samples (TOC-V CSH Shimadzu), particle size distribution by laser beam extinction (HIAC Royco, Pacific Scientific), total coliforms and faecal coliforms quantification by defined substract method (most probable number), *E. coli* both by defined substract method and by membrane filtration, *Clostridium perfringens* and aerobic bacteria at 22˚C by plate counting, algae recount by microscopy counting, *Bacillus* spores, somatic coliphages and F-RNA specific coliphages by plate counting, enterovirus both by plate counting and one step real time polymerase chain reaction (RT-PCR) and norovirus by one step RT-PCR.
Fractionation of DOC was performed by HPSEC using a Toyopearl TSK HW-50S column (250x20 mm) coupled to on-line UV_{254}, organic carbon and organic nitrogen detectors by DOC-Labor (Karlsruhe). It is based on size exclusion liquid chromatography whereby organic compounds are fractionated into five sub-fractions according to their molecular weight (MW): biopolymers, humic substances, building blocks, low molecular weight acids and low molecular neutrals. The organic carbon retained in the chromatographic column (i.e. non-chromatographic DOC) is termed hydrophobic fraction. Further details of each method employed can be found in the corresponding chapter. Membrane feed and permeate streams were analysed on a periodical basis and the lapse time between the sampling moment and the time when the sample was analysed was minimised, keeping the sample under optimal conditions to preserve its characteristics.

A protocol was initially defined for the microbes based membrane integrity tests to ensure the repeatability and the comparability of the results obtained during the two year testing period. Three different bacteriophages were selected for such tests: MS-2, GA and PDR-1, as well as *Bacillus* sp. spores as a control due to its larger size. Bacteriophages were selected because they are similar to enteric viruses since they share many properties with human viruses in terms of composition, structure, morphology and capsid size, they are innocuous to humans and high titers can be obtained in the laboratory. MS-2 and GA present the same size (22 nm) but differ in isoelectric point and hydrophobicity, presenting a different tendency to adsorb onto solids and to aggregate. In particular, they are considered the extreme cases in terms of membranes adsorbability, so that the behaviour of the great majority of human viruses in this respect are in between MS-2 and GA. Therefore, surrogate organisms smaller than the membrane pore size (MS-2 and GA), slightly greater (PDR-1 whose size ranged 60-70 nm) and much larger (*Bacillus* sp. spores length > 1,000 nm; diameter > 500 nm) were used, which provided information on membrane integrity and pore size distribution.

In order to elucidate further impacts of substituting a DWTP conventional pre-treatment by direct UF, a laboratory based RO system was used. The effects of avoiding the dosage of certain chemicals encompassed within the proposed scheme on a RO membrane were studied. RO membrane coupons (Dow Filmtec LE 4040) were exposed to chemical mixtures containing ferric chloride hexahydrate, sodium chlorite, sodium bromide and sodium bisulphite. Rutherford backscattering spectrometry (RBS) was applied to determine the composition of the RO membranes active layer and support with a 2-MeV He+ beam generated with a Van Graaf accelerator (High Voltage Engineering Corp) and its data was fitted using SIMNRA software. The membranes performance in terms of water, chloride and rhodamine-WT rejection was assessed by means of a dead end Amicon cell connected to an analytical balance logged into a computer in order to determine gravimetrically the flux and collect samples for its subsequent quality analyses. Chlorides were analysed by ion chromatography (Dionex IC S-2000 with a Dionex ion Pac As 18 column) and R-WT by fluorescence (excitation/emission wavelengths 550/580 nm) (RF-5301 PC, Shimadzu Scientific Instruments, Inc.). A modified version of the diffusion-solution model which accounts for imperfections in the active layer was used to fit and interpret the RO permeation data (Eq. 7.1, Eq. 7.2). Silver probing experiments were conducted to determine the changes caused by the chemicals exposure on the RO membrane pore size distribution. RBS results were fitted to a bimodal pore size distribution (Eq. 7.3) and the variations of its parameters with respect to the virgin membrane enabled understanding the permeation results obtained.

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CHAPTER 2

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

This chapter is based on:

Ferrer, O., Lefèvre, B., Prats, G., Bernat, X., Gibert, O., Paraira, M., (in press) Reversibility of fouling on ultrafiltration membrane by backwashing and chemical cleaning: differences in organic fractions behaviour. Desalin. Water Treat. In press

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Abstract

The substitution of a part of a drinking water treatment plant (DWTP) conventional pre-treatment (sand filtration) by ultrafiltration (UF) was covered in this chapter. A bench scale outside-in hollow fibre UF (80 nm) module operated under dead end filtration mode at constant transmembrane pressure was employed. The capability of continuously operate the UF system with real settled water of a DWTP was demonstrated and the high and consistent water quality produced verified its suitability.

Because of the impact of membrane fouling on the feasibility of membrane based processes, this chapter addressed multiple variables linked to backwashing (BW), the cleaning operation performed more frequently, in order to optimise its performance. The effect of BW transmembrane pressure, duration, frequency and composition on the reversibility of UF membrane fouling and on the permeate quality (concerning total organic carbon, turbidity and UV absorbance) was studied. Results showed that in general the more intensive a 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 (i.e. the chemically enhanced backwash (CEB)), 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 of the total resistance over time.

The organic fractions most removed by the membrane and, of these, which were most detached after BW, alkaline and oxidant cleaning in place (CIP) and acid CIP episodes were determined. 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.

2.1. Background

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 (Crozes et al., 1997, Decarolis et al., 2001, Lee et al., 2008, Wang et al., 2008, Ye et al., 2010).

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 of the energy consumption of the process, lowering of the productivity, worsening of the product quality and eventually premature replacement of membranes (Katsoufidou et al., 2005, Kim and DiGiano, 2006, Lee et al., 2008, Wang et al., 2008).

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 (Katsoufidou et al., 2005, Kim and DiGiano, 2006, Remize et al., 2010, Yang et al., 2011). 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 of the resistance (with the subsequent increase of 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). Figure 2.1 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}).

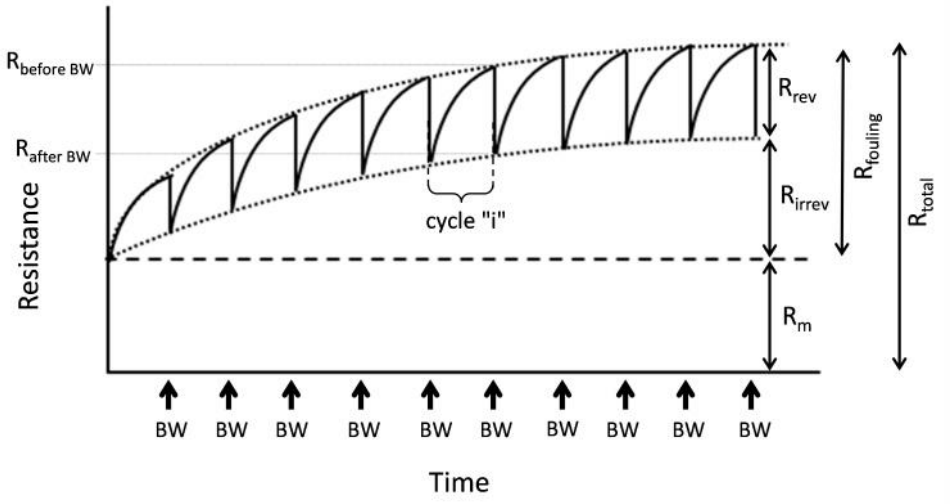

Figure 2.1. Qualitative representation of the evolution of membrane resistance over a succession of filtration and backwashing (BW) cycles.

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 (Chen et al., 2003, Crozes et al., 1997). 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) (Zheng et al., 2011). This cleaning operation does not require an extended shutdown, since it is conducted on line, and the chemical 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 is largely dependent on multiple variables such as membrane characteristics, feed water properties, filtration conditions, module configuration, BW regime… making the control of membrane fouling a complex phenomenon. Among these, the effect of feed water composition and membrane operating conditions have been most researched (Katsoufidou et al., 2005, Li et al., 2009, Lin et al., 2009, Peldszus et al., 2011), while less studies have dealt with the effect that BW variables (duration, frequency…) 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 (Chen et al., 2003, Decarolis et al., 2001, Kim and DiGiano, 2006, Wang et al., 2008, Yun et al., 2011, Zheng et al., 2011), seawater (Li et al., 2012, Pervov et al., 2003, Ye et al., 2010) and surface water (Crozes et al., 1997, Remize et al., 2010)), each with different fouling behaviour potential 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 (Ye et al., 2010). Second, the configuration of UF modules in these studies is very variable: flat-sheet (Remize et al., 2010), spiral wound (Pervov et al., 2003), pressurised (inside-out) (Decarolis et al., 2001, Kim and DiGiano, 2006, Li et al., 2012, Zheng et al., 2011) and submerged (outside-in) (Remize et al., 2010, Ye et al., 2010) hollow fibre membrane systems, also affecting the propensity to fouling (Fratila et al., 2001, Ye et al., 2010, Yun et al., 2011). Furthermore, most of them are focused on the evolution of the membrane resistance and fouling rates (Crozes et al., 1997, Decarolis et al., 2001, Kim and DiGiano, 2006, Wang et al., 2008, Yun et al., 2011) and only a few quantify the reversible and irreversible fouling after each backwash cycle (Ye et al., 2010). 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 (Haberkamp et al., 2008, Henderson et al., 2010, 2011). 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 (Huber et al., 2011).

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 backwashing (BW) and cleaning-in-place (CIP) episodes. For this purpose, a bench scale outside-in hollow fibre UF 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.

2.2. Materials and methods

2.2.1. Feed water characteristics

The feed water to be filtered by the UF module was decanted water from the settling basin of the DWTP in Sant Joan Despí (Barcelona, Spain). The average composition of this water during the course of the study is given in Table 2.1.

Table 2.1. Average feed water quality (SJD DWTP settled water). Confidence intervals at a confidence level of 95% for all cases. Number of analysed samples: 75 (for pH, conductivity, turbidity and UV_{254}) and 14 (for TOC, Al, Fe and P).

Parameter (units)	Concentration
pH	7.6±0.1
Conductivity (µS/cm)	1490±160
Turbidity (NTU)	1.76±0.19
UV_{254} (cm^{-1})	0.080±0.006
TOC (mg/L)	4.1±0.24
Al (µg/L)	364±51
Fe (µg/L)	23±9
P (µg/L)	43±14

2.2.2. UF device and membrane characteristics

All experiments conducted in this study were carried out employing a bench scale outside-in hollow fibre UF 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 2.2.

Table 2.2. Characteristics of the UF membrane module provided by the manufacturer.

Membrane characteristics	
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 (m²)	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 (ºC)	35
pH range	2-12

The decanted feed water was directed to the UF module by means of a centrifugal pump (IML S.A.U., Model MS100M). 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 Figure 2.2.

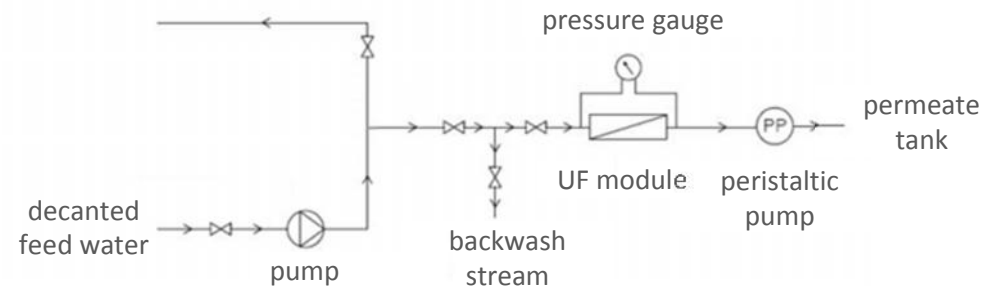

Figure 2.2. Schematic diagram of the experimental UF system setup.

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 2.2.6.

Each filtration experiment was carried out at a filtration TMP of 1.2 bar and one combination of BW related variables, i.e.: backwash TMP (BW_{TMP}), backwash duration (BW_d), backwash frequency (BW_f) and chemically enhanced backwash 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 2.3) while setting all other variables at fixed values (marked in bold in Table 2.3). 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.

Table 2.3. 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

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

Permeate flux and quality was 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 experiments was taken from the same location in the treatment train of the DWTP in Sant Joan Despí, the differences observed in fouling reversibility could be attributed to the investigated BW related variables.

2.2.4. 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 backwashing 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 3 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, contact time 30 min). The reagents used for CIP-B and CIP-A were selected in accordance with the ones used in the DWTP 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.

2.2.5. 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 (250x20 mm) coupled to on-line UV_{254}, organic carbon (OC) and organic nitrogen (ON) detectors by DOC-Labor (Karlsruhe). The principles of the technique are reported in depth by Huber et al. (2011). 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 organic carbon retained in the chromatographic column (i.e. non-chromatographic DOC) is termed 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.

2.2.6. Data treatment for the membrane hydraulic performance evaluation

Fouling was determined by the increase of resistance posed by the fouled membrane, which was in turn calculated from the decline of permeate flux according to the well-established Darcy's equation (Eq. 2.1):

$$J = \frac{\Delta P}{\mu \cdot R_{total}} \qquad \text{Eq. 2.1}$$

where J is the permeate flux ($m^3 \cdot m^{-2} \cdot s^{-1}$), ΔP is the TMP (bar), μ is the permeate viscosity (bar·s) (corrected to 20ºC) 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 by Eq. 2.2 (Lee et al., 2008, Peldszus et al., 2011, Remize et al., 2010):

$$J = \frac{\Delta P}{\mu \cdot (R_m + R_{rev} + R_{irrev})} \qquad \text{Eq. 2.2}$$

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^i_{rev} was calculated as the difference of resistance measured before and after backwashing (Eq. 2.3, as shown in Figure 2.1).

$$R^i_{rev} = R^i_{before\ BW} - R^i_{after\ BW} \qquad \text{Eq. 2.3}$$

The contribution of R^i_{rev} over the total fouling of the membrane ($R_{fouling}$) can then be calculated as shown in Eq. 2.4 (see Figure 2.1):

$$\text{Reversible fouling}\ (\%) = \frac{R^i_{rev}}{R^i_{fouling}} = \frac{R^i_{before\ BW} - R^i_{after\ BW}}{R^i_{before\ BW} - R_m} \qquad \text{Eq. 2.4}$$

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 e.g. initial fouling on fouling evolution. For this reason, measured fouling related variables were not normalised and reported as measured.

2.3. Results

Plotted in Figures 2.3 - 2.6 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. 2.2, 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 Figure 2.1, 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 the BW regime, irreversible foulants slowly accumulated onto and into the membrane.

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

As shown in Figure 2.3, higher BW_{TMP} provided a lower resistance increase (i.e. a better permeability restoration) over the experiment (Figure 2.3a) and a higher degree of fouling reversibility (Figure 2.3b). R_{rev} percentage was below 30% at BW_{TMP} of 0.7 and 1.0 bar, but it increased to 31% at BW_{TMP} of 1.5 bar and up to 41% at BW_{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 BW_{TMP}.

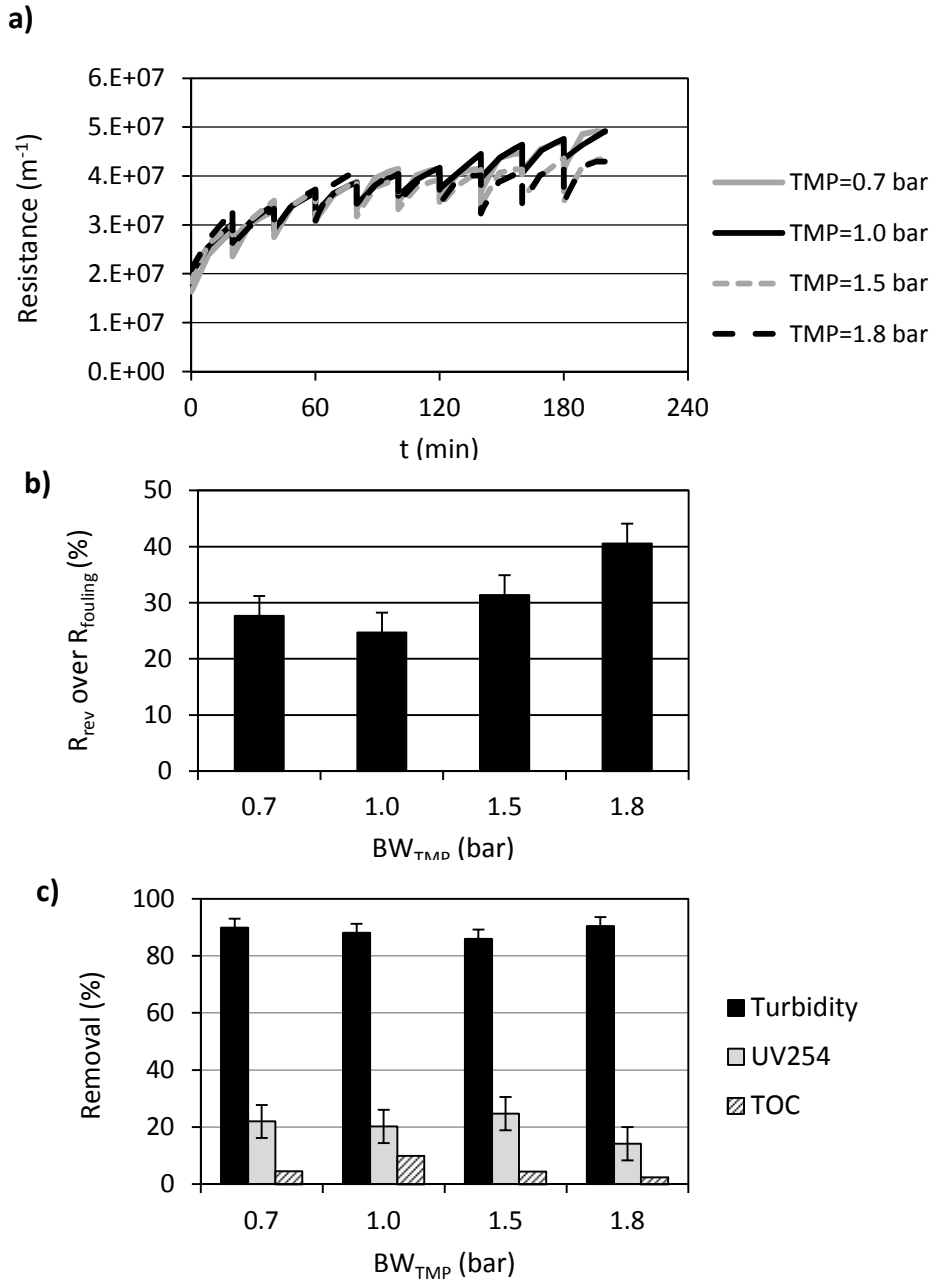

Figure 2.3. Effect of backwash transmembrane pressure (BW_{TMP}) on the a) total resistance of the fouled membrane, b) percentage of reversible fouling over the total membrane fouling and c) removal of turbidity, UV_{254} and TOC by the UF membrane. Error bars correspond to confidence intervals at a confidence level of 95% for all cases.

This finding is partially in accordance with that reported by Remize et al. (2010), who observed that increasing BW_{TMP} from 1.2-2.0 bar in the filtration of surface water with UF membranes resulted in an increase of 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 of permeability recovery with BW_{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 regards to the permeate quality, removal of turbidity, UV_{254} and TOC were comparable within the experimental error whatever the BW_{TMP} applied (Figure 2.3c). Turbidity was decreased at a high degree (average removals of 89%), while UV_{254} and TOC were decreased by 20% and 5% for all BW_{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 MW ≤ 1,000 Da (see section 2.3.5), much smaller than the nominal MWCO of the UF membrane (300,000 Da, see Table 2.2).

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 Figure 2.4. It is noticeable in Figure 2.4a that the initial resistance for BW_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, backwashing every 10 min resulted in a lower fouling rate, in contrast to backwashing 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 Figure 2.4b, 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 differ considerably if other types of feed water or UF configurations are used as it is commonly the case (Decarolis et al., 2001, Wang et al., 2009, Zheng et al., 2011). 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 (Kim and DiGiano, 2006, Ye et al., 2010, Yun et al., 2011).

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 that of UV_{254} and TOC was only 15% and 5%, respectively.

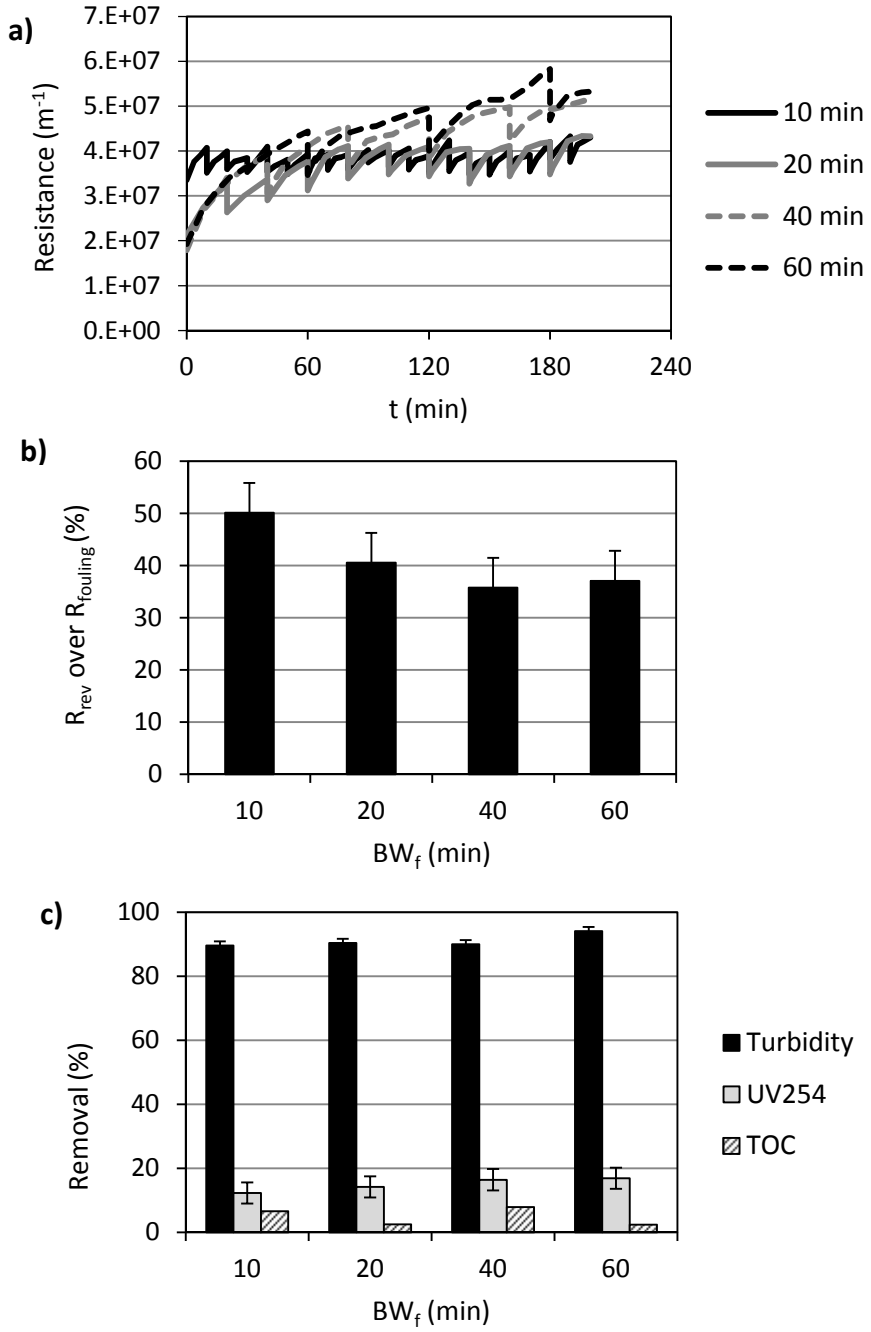

Figure 2.4. Effect of backwash frequency (BW_f) on the a) total resistance of the fouled membrane, b) percentage of reversible fouling over the total membrane fouling and c) removal of turbidity, absorbance and TOC by the UF membrane. Error bars correspond to confidence intervals at a confidence level of 95% for all cases.

2.3.3. 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 Figure 2.5. As in the previous set of experiments, an experiment showed an initial membrane resistance slightly higher than the corresponding to the other experiments, suggesting again that the membrane was not completely cleaned prior

to the filtration experiment. Despite the different starting point, the evolution of resistance over all experiments is comparable.

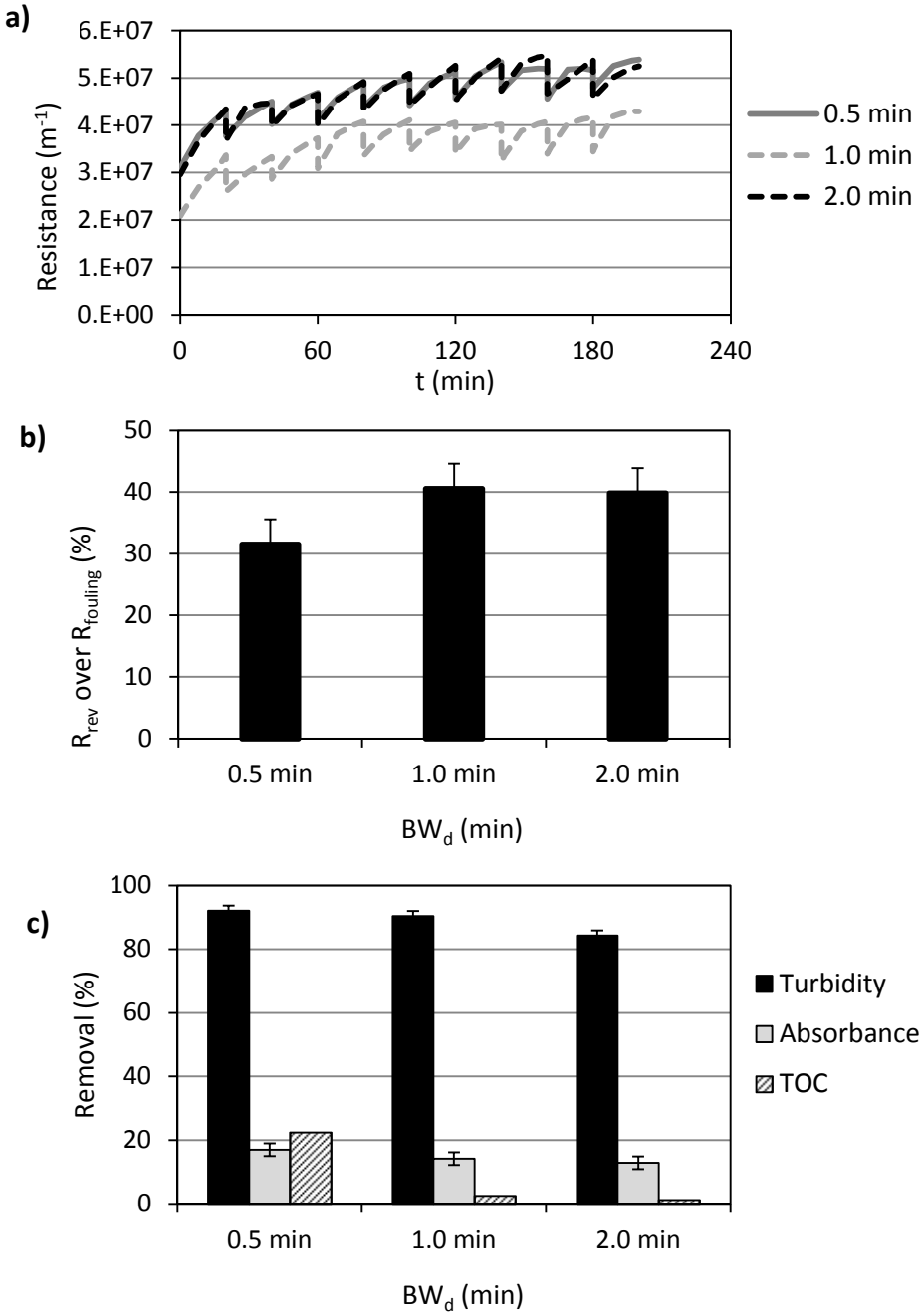

Figure 2.5. Effect of backwash duration (BW_d) on the a) total resistance of the fouled membrane, b) percentage of reversible fouling over the total membrane fouling and c) removal of turbidity, UV_{254} and TOC by the UF membrane. Error bars correspond to confidence intervals at a confidence level of 95% for cases.

Increasing BW_d from 0.5 min to 1.0 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 (Figure 2.5b). In fact, better fouling removal from UF membrane at increased BW_d has been reported in the scientific literature for very variable filtration scenarios in terms

of feed water characteristics and UF configurations (Decarolis et al., 2001, Kim and DiGiano, 2006, Li et al., 2012, Pervov et al., 2003, Wang et al., 2008, Ye et al., 2010, Yun et al., 2011), including other types of membrane systems such as microfiltration (Yang et al., 2011), ceramic membranes (Hwang et al., 2009) and membrane bioreactors (Yigt et al., 2009).

In our study, lengthening the BW_d to 2.0 min was not accompanied by any increase of fouling reversibility. The existence of a threshold in BW_d beyond which no further improvement is observed has also been observed by other researchers (Huber et al., 2011, Ye et al., 2010). Ye et al. (2010) 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).

2.3.4. Effect of the chemically enhanced BW composition ($BW_{CEB\text{-}c}$)

The fouling rate and reversibility degree differed depending on the chemical cleaners used for the CEB (Figure 2.6). 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%) (Figure 2.6b).

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 (Arnal et al., 2009) and wastewater (Nguyen and Roddick, 2011, Zheng et al., 2011), while NaOH had less influence compared to water. Similar results were observed by Espinasse et al. (2012) 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 (Liu et al., 2000, Porcelli and Judd, 2010, Zheng et al., 2011,). To exemplify the disinfection power of some chlorine based compounds, Laîné et al. (1991) reported that ceasing the dosage of chlorine in backwash water after 20 days of operation resulted in severe fouling of the membranes within 5 days. 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 (Porcelli and Judd, 2010).

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 (Liu et al., 2000, Porcelli and Judd, 2010, Strugholtz et al., 2005). However, the combination of NaClO and NaOH

in this study did not perform better than NaClO alone (Figure 2.6). 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.

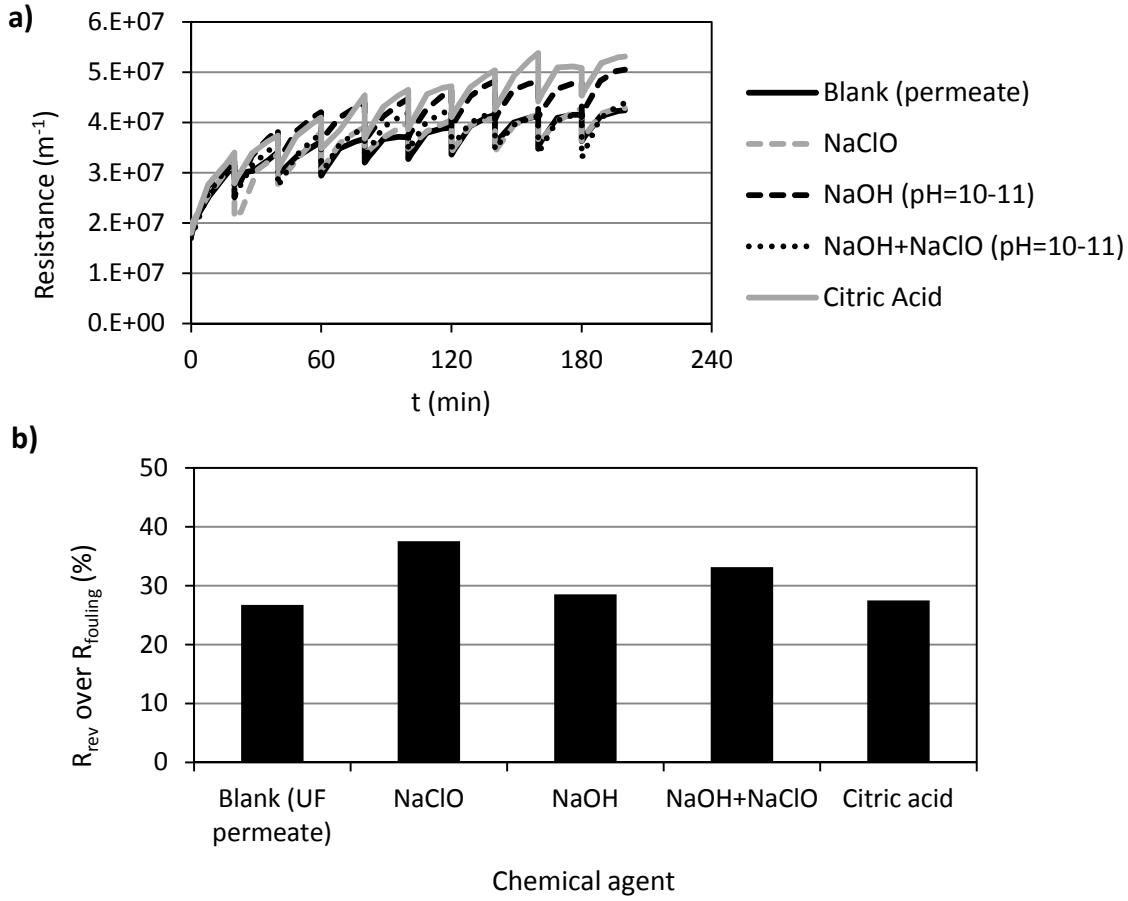

Figure 2.6. Effect of the CEB composition ($BW_{CEB\text{-}C}$) on the a) total resistance of the fouled membrane, b) percentage of reversible fouling over the total membrane fouling by the UF membrane (confidence intervals ≤4.0% at a confidence level of 95% for all cases).

2.3.5. Organic fouling composition on the UF membrane

Figure 2.7 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, respectively. This difference (of 15%) indicated that after the coagulation/decantation stage a fraction of the organic load was still in the form of particular or colloidal organic carbon. With regards 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 (Haarhoff et al., 2010, Velten et al., 2011).

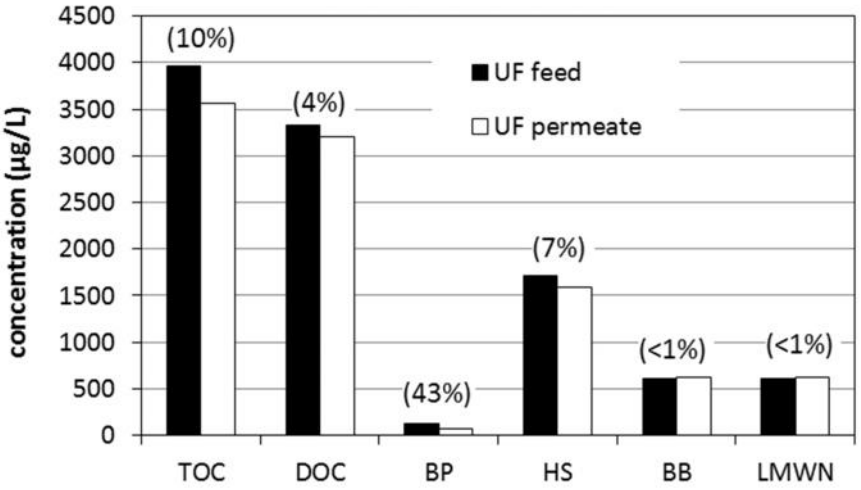

Figure 2.7. Concentration of TOC, DOC and its fractions BP, HS, BB and LMWN in both feed and permeate streams (in brackets removal percentages by UF the membrane).

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 (Haberkamp et al., 2011, Henderson et al., 2011, Lee et al., 2004, Peter-Varbanets et al., 2011, Tian et al., 2013).

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 ultrafiltration of water (Henderson et al., 2011).

2.3.6. Fouling detachment after backwashing 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) than ultrafiltered water used for the backwash (3.6 mg/L). 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.

Figure 2.8 compares the initial organic mass (in µg) fouling the UF membrane with the mass remaining after applying BW (+CEBs) and CIP-B 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 ultrafiltration of a municipal activated sludge effluent (Nguyen and Roddick, 2011). 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 (Katsoufidou et al., 2005, Laîné et al., 1991, Nguyen and Roddick, 2011). The remaining BP and HS on the membrane would explain the irreversible fouling (never completely avoided whatever the BW regime applied) that resulted in the gradual increase of total resistance over time (Figures 2.3 - 2.6). 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) (Figure 2.7). HS is considered by some studies of minor relevance in terms of fouling due to their high transmission through the mesoporous UF membrane (Haberkamp et al., 2011, Henderson et al., 2011, Peter-Varbanets et al., 2011), whereas it is considered a detrimental foulant causing severe hydraulically irreversible fouling by some others (Jermann et al., 2007, Yuan and Zydney, 2000).

Opposite to HS, BP was found to be the most retained fraction in terms of percentage (but not of amount) (Figure 2.7), in agreement with other previous studies (Haberkamp et al., 2008, Henderson et al., 2011). 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 (Haberkamp et al., 2011, Henderson et al., 2010). 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 (Haberkamp et al., 2011). 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) (Figure 2.8).

In this study, because a portion of both BP and HS fractions were 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.

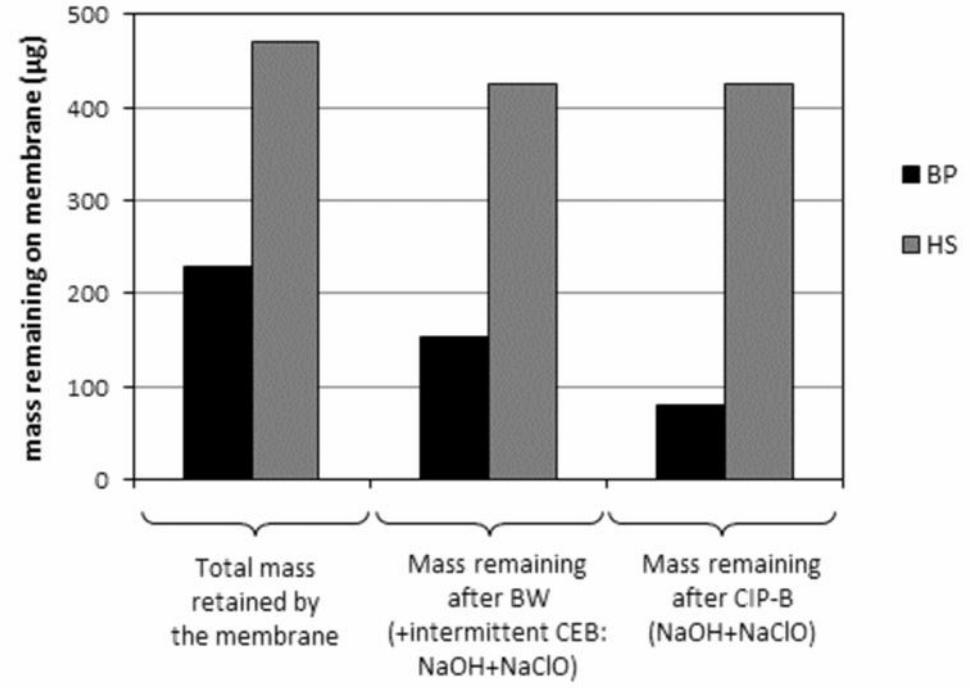

Figure 2.8. Evolution of mass of BP and HS remaining on the UF membrane (µg) after the successive application of BW (+intermittent CEB: NaOH+NaClO) and CIP-B (NaOH+NaClO).

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 not easily detached by NaOH either 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, 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 (Porcelli and Judd, 2010). 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 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) (Strugholtz et al., 2005). This is in qualitative agreement with Strugholtz et al. (2005), who found that NaOH and in particular NaClO were effective at removing both BP and HS while HCl was not (Strugholtz et al., 2005). 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.

2.4. 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 of 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 a 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 for the considered water stream, 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 regards to the permeate quality, no significant differences were observed whatever the BW regime applied. Turbidity removal was always above 88%, whereas UV_{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 (SDI) 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 regards 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 (Henderson et al., 2011, Lee et al., 2004, Tian et al., 2013). 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 induce 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 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.

2.5. Conclusions

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

- Irreversible fouling was never completely avoided whatever the BW regime applied, resulting in a gradual increase of total resistance over time.
- The degree of reversibility depended on the BW related variables: the more intensive a 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.
- Under all BW conditions assessed, turbidity removal was above 88%, whereas UV_{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.
- 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.
- 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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CHAPTER 3

Pre-treatment of Llobregat River raw water through pressurised inside/out hollow fibre ultrafiltration membranes

This chapter is based on:

Ferrer, O., Serrallach, X., Horváth, F., Mesa, J., Gibert, O., Bernat, X., 2013. Pre-treatment of Llobregat River raw water through pressurized inside/out hollow fibre ultrafiltration membranes. Desalin. Water Treat. 51, 1831–1837

DOI: 10.1080/19443994.2012.714637

Abstract

The feasibility of raw river direct ultrafiltration, as an alternative to the whole conventional pre-treatment (dioxichlorination, coagulation/flocculation, settling and sand filtration) of a drinking water treatment plant, was investigated at prototype scale (May–October 2011). A highly variable and challenging water resource was selected, in order to assess different scenarios, covering a broad range of conditions. The prototype was able to deal with conditions ranging from 20 to >800NTU successfully, without any chemical pre-treatment and consuming low amount of chemical reagents for cleaning purposes. The membranes performance proved to work better in terms of water production yield and resistance build up stability at medium and high turbidity episodes than at lower ones, probably due to a cake layer formation which prevented small binding organic species and particles reaching the membrane. Permeate quality, both in microbiological and most of physico-chemical terms, was independent of the feed water characteristics.

3.1. Background

Drinking water treatment plants (DWTPs) will have to face significant challenges in the following decades. On one hand, they will have to be able to supply an increasing water demand. On the other, it is likely that water resources (DWTPs' feed) will present a lower quality and therefore water treatment units will need to be modified accordingly. Additionally, other aspects will have to be taken into account: legislation, increasing energy cost and social requirements in terms of processes sustainability. In the legislative aspects side it is worth mentioning that it is becoming more stringent both in terms of product water as well as the process itself. For instance, the Spanish Order SAS/1915/2009 bans certain chemicals, such as polyacrylamides, frequently used in coagulation/flocculation pre-treatments. As a result, technologies capable of successfully achieving legislative, environmental and social challenges in a sustainable way are urgently needed.

Membrane technology has significantly evolved in the last decades, becoming a technological solution increasingly applied in DWTPs (Pressdee et al., 2006) due to its advantages. In particular, low pressure membrane systems, including microfiltration (MF) and ultrafiltration (UF), are being increasingly used for drinking water production as final treatment sequence (Guo et al., 2010) and have gradually gained acceptance as the preferred pre-treatment to reverse osmosis (RO) (Pearce, 2008). This work aims at demonstrating at prototype scale the feasibility of applying direct UF (i.e. direct raw water filtration by UF) instead of the conventional pre-treatment (dioxichlorination, coagulation/flocculation, settling and sand filtration). The case study selected is the Llobregat River, in Barcelona (Spain) a challenging scenario because of its large water variability in terms of quality and quantity.

Few previous works published have assessed the evaluation of direct MF/UF as alternatives to conventional pre-treatment in DWTPs treating surface water, concluding that they are suitable alternatives in terms of quality (Hofman et al., 1998, Rojas et al., 2008, Xia et al., 2004). Nonetheless, the scale of the experiments reported by these studies (bench level), duration (few months) or feed water qualities (canal or reservoir water) were highly different from the ones covered in this study. Turbidities of the feed water in these previous studies (around 20 NTU, with a maximum of 150 NTU) were well below the average of the Llobregat River (average of 171 NTU and a maximum value of >800 NTU, for the period considered). As a result, the feasibility of direct UF is not proved yet at these extreme feed water quality conditions. The objective of this work was to study at prototype scale the feasibility of direct UF with pressurised inside/out hollow fibres of highly variable raw surface water, characterising their performance in different water quality scenarios.

3.2. Materials and methods

The Llobregat River is the main surface water resource of Barcelona metropolitan area (North East of Spain) and it is characterised by its Mediterranean behaviour: large flow fluctuations (severe droughts during summer and flash flood events in spring and autumn) and its associated water quality variations. Moreover, the Llobregat River suffers from historical industrial and urban contamination (Hutzinger, 2012).

The direct UF prototype plant used in this work treated raw Llobregat River water, which exhibited fluctuations between 20 and >800 NTU (maximum reading limit) during the tested period (May-October 2011), without any chemical pre-treatment. The prototype was equipped with a strainer (300 µm) as mechanical pre-treatment to prevent excessive clogging of the subsequent inside-out pressurised hollow fibres (Pentair X-Flow Aquaflex - polyethersulfone membranes with a nominal pore size of 0.020 µm and 0.8 mm of internal fibre diameter), and was controlled automatically by a Scada system. The software enabled the modification of several variables, such as filtration time, permeate flow, cleaning conditions (frequency, duration, backwash flow, air flow, reagents nature and concentration), etc. so that the prototype was adaptable to the changing conditions when necessary.

The prototype initially worked under 30 minutes of filtration time treating 3.3 m^3/h (60 L/(m^2·h)) at constant permeate flow, followed by a hydraulic cleaning (HC) (initial forward flush [62.5 L/(m^2·h), 20 s], backwash [250 L/(m^2·h), 20 s] enhanced by airflush [10 Nm^3/h, 10 s] and final forward flush [62.5 L/(m^2·h), 40 s]). Every 50 filtration cycles, a chemically enhanced backwash (CEB) was undertaken, composed of a basic-oxidising stage (NaOH and NaClO) and an acid stage (HCl) subsequently. The CEB sequence consisted of HC, dosing [125 L/(m^2·h), 45 s], soaking [10 min] and rinsing [250 L/(m^2·h), 45s] stages. Alkaline solution concentration was 480 mg/L, oxidiser 200 mg/L and acid 438 mg/L. In August 2011, filtration time was decreased to 15 minutes and in order to maintain one CEB per day approximately, the CEB was conducted every 100 filtration cycles.

When a pre-set value of recoverable resistance was reached ($1.4E^{+12}$ m^{-1}), a HC was automatically performed, shortening the filtration time but restoring membranes resistance. If high resistance was reached in less than 10 minutes of filtration time, the prototype plant was automatically stopped, as a safety measure, to avoid situations of continuous HCs. Also, if a higher pre-set value of recoverable resistance ($1.8 \cdot 10^{12}$ m^{-1}) was achieved almost immediately after starting filtration, the prototype stopped.

Specific cake resistance (α), which represents the increase of the cake layer resistance build up with filtered volume, was calculated as shown in Eq. 3.1. Membrane resistance (R) during a filtration cycle was approximated to a first order polynomial and then it was derived respective to the specific volume (v) (i.e. filtered volume per unit area).

$$\alpha = \frac{dR}{dv} = \frac{dR}{d(V/A)} \qquad \text{Eq. 3.1}$$

Both Llobregat River water and membrane permeate stream were characterised by different analyses in a periodical basis. The parameters monitored and the methods used were: temperature by resistivity (Endress&Hausser TR10-ABG1HDSAG2000), conductivity by electrometry (Endress&Hausser CLS21D-C1+CM42-KAA000EAN00), pH by potenciometry (Hach-Lange DPD1P.99), turbidity by nephelometry (Hach-Lange Ultraturb SC), total suspended solids (TSS) by ESS 340.2, absorbance at 254nm (UV_{254}) by spectrophotometry (Hach-Lange DR 5000), silt density index (SDI_{15}) by ASTM D4189 (Simple SDI Meter 9C-281-0157), dissolved organic carbon (DOC) by combustion-infrared method using a DOC analyser (non-purgeable organic carbon, UNE-EN 1484), after filtration with a 1.2 µm glass fibre filter for the raw water

samples (TOC-V CSH Shimadzu), total coliforms, faecal coliforms and *E. coli* quantification by the defined substract method (most probable number), *Clostridium perfringens* and aerobic bacteria at 22ºC by plaque counting, and algae count by counting chamber.

3.3. Results and discussion

3.3.1. *Hydraulic response*

Figure 3.1 shows the membrane resistance evolution (temperature corrected) along time (from May 2011 to October 2011) (black symbols), as well as the raw water turbidity fluctuation (grey symbols). Despite the large variability of the latter (from 20 to >800 NTU), the prototype proved to be able to treat the raw river water without any chemical pre-treatment. Nevertheless, its hydraulic performance varied during the different turbidity periods faced. Long term prototype shutdown, mainly due to external factors such as feed pumping problems, electrical power failure, etc. led to periods where no data was generated and hence, resistance and turbidity data is not available in Figure 3.1.

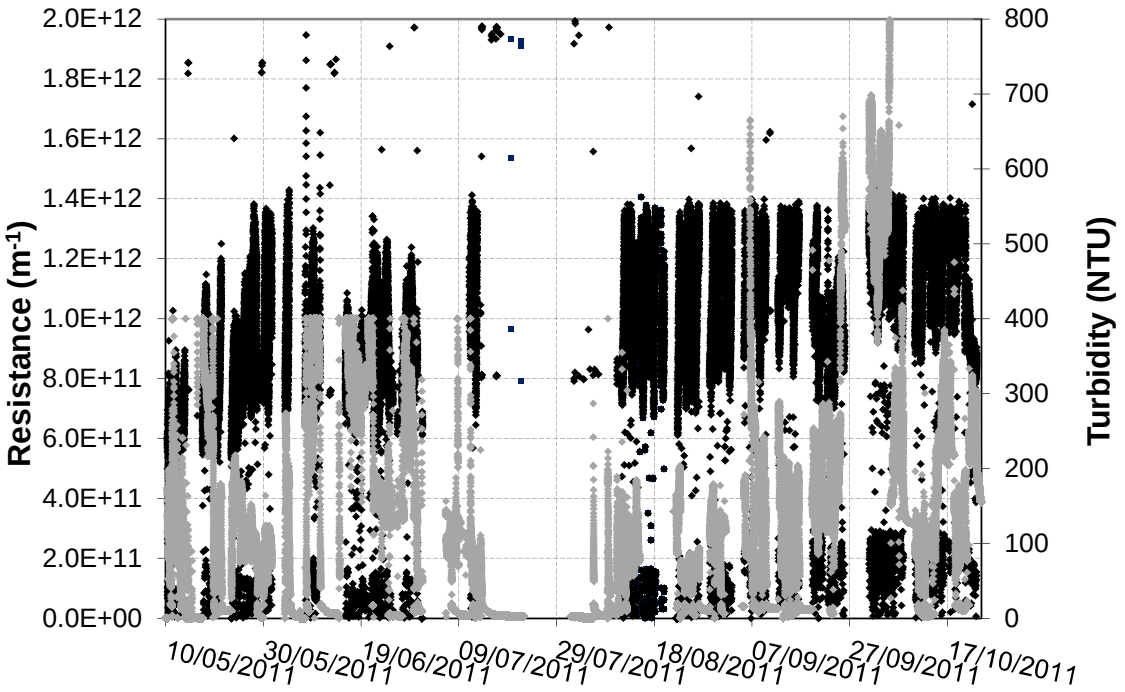

Figure 3.1. Membranes' resistance (temperature corrected) and raw river water turbidity evolution along time (May – October 2011). Black symbols correspond to membrane resistance whereas grey symbols turbidity values. Until July, turbidity maximum reading scale was set on 400 NTU, afterwards on 800 NTU.

Generally, at greater turbidity (150-250 NTU approximately) the prototype suffered less interruptions caused by exceeding the pre-set value for recoverable resistance than at lower turbidity. Filtration time was sometimes reduced automatically by the control system when reaching the pre-set resistance value ($1.4E^{+12}$ m^{-1}), but not being less than 10 minutes, which

would have led to the prototype stop. This can be seen in Figure 3.2, where filtration time (dark symbols) is plotted versus raw river water turbidity (grey symbols). As stated, when raw river turbidity ranged between 150 and 250 NTU, filtration time was normally equal to the filtration time set point (30 minutes), so that the membrane resistance was below the pre-set resistance value and the production water yield was maintained (HC were not conducted before the filtration time fixed). On the contrary, periods with lower raw river turbidity, filtration time was automatically reduced because high resistance pre-set value was achieved, so that the prototype conducted HCs more often, to such an extent that when it was less than 10 minutes, the prototype stopped, as programmed. In August 2011, when turbidity was lower than 150 NTU, to minimise prototype stops, filtration time was reduced to 15 minutes, minimum filtration time to 4 min and CEB frequency increased to 100 filtration (to keep chemical cleaning conditions constant), but filtration flow was not modified (to maintain hydraulic conditions). However, at that point turbidity increased significantly, leading to very high turbidity episodes (>250 NTU). In this case, filtration time also decreased significantly (and hence HC were performed more frequently) by reaching high resistance threshold, but the prototype did not stop, since the time needed to achieve this value was greater than 4 min.

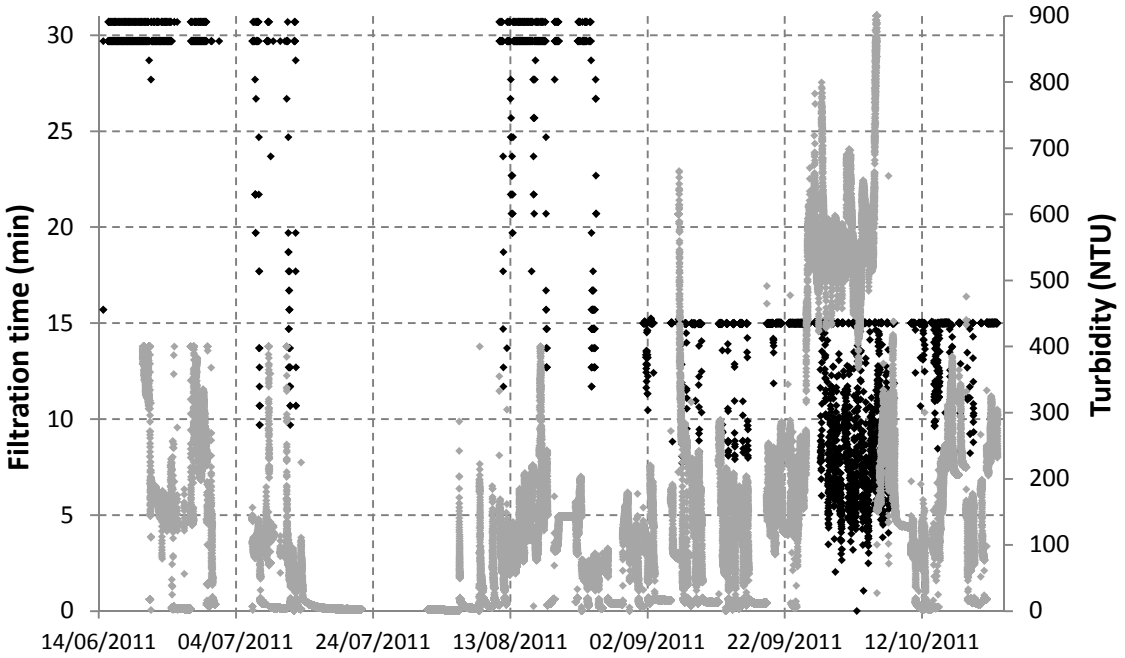

Figure 3.2. Filtration time (dark symbols) and turbidity (grey symbols) along time (June – October 2011). Until July, the turbidity maximum reading scale was set on 400 NTU, afterwards on 800 NTU.

Figure 3.3 presents the specific cake resistance (calculated by Eq. 3.1) along time (dark symbols) as well as turbidity evolution (grey symbols). Low turbidity episodes (<150 NTU) induced a greater resistance build up than medium turbidity schemes (150-250 NTU), leading to a faster achievement of the resistance pre-set value and hence, a reduction in filtration time.

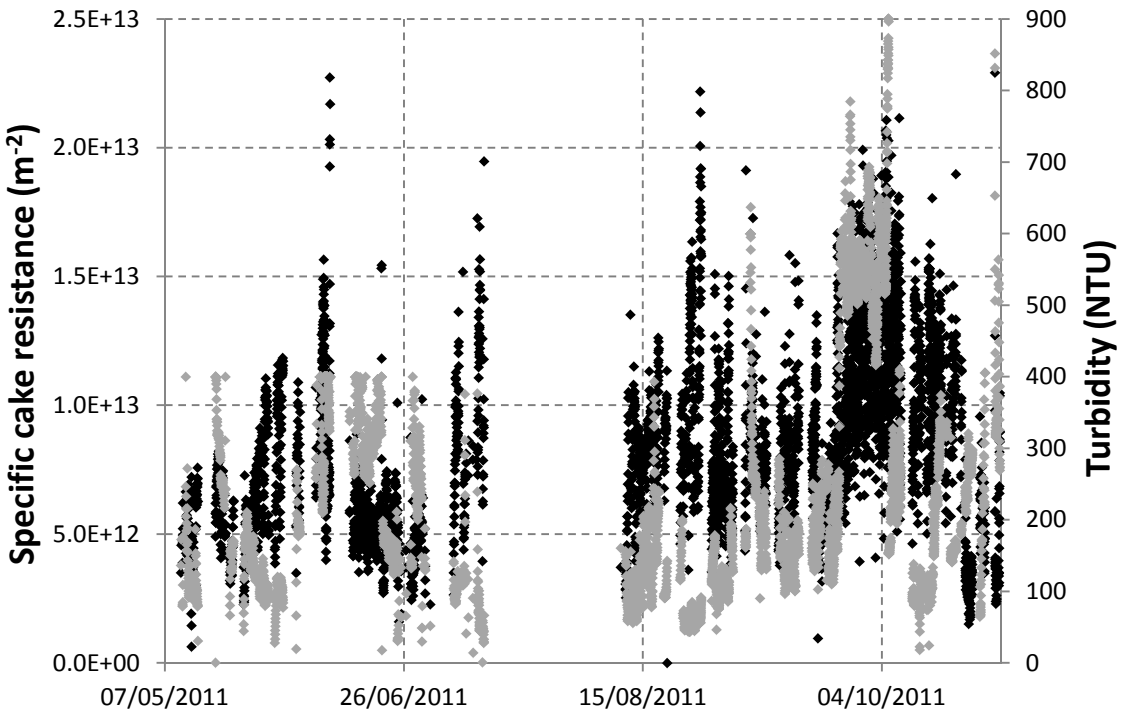

Figure 3.3. Specific cake resistance (calculated by Eq. 3.1) (dark symbols) and turbidity (grey symbols) along time (May – October 2011). Until July, the turbidity maximum reading scale was set on 400 NTU, afterwards on 800 NTU.

Several parameters affect specific cake resistance, among them particle shape, size distribution, porosity, particle density and TSS (Listiarini et al., 2009, McCarthy et al., 2002, Sripui et al., 2011). As remarked, the episodes where greater specific cake resistance was faced by the membrane in this work were when raw water presented low turbidity and extremely high turbidity (Figure 3.3). Based on Carman-Kozeny equation (Mulder, 1991), the first scenario may be explained either by low particle density, low cake porosity and/or small particles diameter. In the case of very high turbidity events, a similar behaviour was described by Sripui et al. (2011), who found that specific cake resistance increased with TSS concentration for a certain particle size range (1-20 μm).

Natural organic matter (NOM) is generally recognised as the main UF organic foulant, and recently it has also been suggested to play a detrimental role in inorganic particle fouling (Jermann et al., 2008). Nonetheless, the effects of NOM on inorganic particles stabilisation reported in the literature are different according to the NOM fraction considered (humic substances and polysaccharides, especially) and sometimes contrary results are reported (Chen et al., 2006, Labille et al., 2005, O'Melia and Tiller, 1993, Shimm and Morgan, 1995). Extracellular polymeric substances (EPSs), which are mainly polysaccharides, proteins, glycoproteins and glycolipids (Flemming and Wingender, 2007), and in particular, transparent exopolymer particles (TEPs) have been recently identified as important fouling agents in UF (Bar-Zeev et al., 2009, Villacorte et al., 2009a). It has been stated that they may not only be responsible for biological or organic fouling but may also enhance colloidal/particulate fouling

(Villacorte et al., 2009a). Therefore, the differences in behaviour observed in this study may be due to an increase in TEPs content in raw water. Villacorte et al. (2009b) analysed TEPs evolution in seawater and the greater concentration was found during spring and early summer (March, April) rather than in August, as found here. Nevertheless, this hypothesis cannot be discarded since the North Sea seawater and Llobregat River composition as well as climate characteristics from the Netherlands and Spain are significantly different.

The interactions between NOM and particles are not sufficiently known and they may be one of the causes of the differences in the membranes behaviour identified during low, medium and high turbidity episodes.

During high turbidity episodes, the higher particles content or the shifts in particle size distribution may lead to a cake layer formation, preventing small organic molecules reaching the membrane and thus, minimising pore constriction and/or blockage. The latter have been identified in the literature as the most detrimental fouling mechanism in terms of flux decline (Boerlage et al., 1998, 2002, Hong and Elimelech, 1997, Lin et al., 2000. As stated, greater particles content may lead cake formation as the main fouling mechanism and thus, act as an additional filtration barrier preventing small adsorptive particles, susceptible of binding in the membranes surface and/or porous structure, reaching the membrane (Blankert et al., 2007). Particulate cake formed may exhibit a greater average porosity, inducing lower membranes resistance according to Carman-Kozeny equation (Mulder, 1991, Jermann et al., 2008). Moreover, a cake layer formed by bigger particles presents a lower resistance than one of smaller particles, assuming equal weights of small and big particles, equal rejection and interactions among them and the membrane (Kim and Hoek, 2002, Carroll et al., 2000). Additionally, NOM has been identified by several researchers as glue, binding inorganic particles to one another and to the membrane surface. In water matrixes containing high inorganic particles concentration, NOM may not be able to link to all the particulate matter among it and/or to the membrane, leading to a less compact cake and/or less tightly linked and hence, resistance.

During low turbidity periods, since less particulate matter is contained in raw water, cake formation may not be so important and either more low molecular weight organics may reach the membrane and cause pore constriction/blocking or the cake formed may be more compact because there is a greater NOM/particulate ratio (assuming NOM content is constant, since the DOC does not change significantly in the tested water) and, as a result, NOM binding to particles and/or the membrane is probably more prominent.

Both cake formation and its porosity may explain why the membrane performance is more stable and hence, presents fewer shutdowns due to high resistance, at greater turbidity periods than lower ones.

According to Carroll et al. (2000) and Lin et al. (2000), coagulation reduces fouling rate, since it transforms dispersed particles and other organic and/or inorganic pollutants into more retainable forms (Sundaramoorthy et al., 2005) by charge neutralisation and flocculants sweep (Gao et al., 2011). Microflocs formed progressively grow in size turning into macroflocs,

leading to more permeable fouling layer and/or preventing pore blockage (Sundaramoorthy et al., 2005). Coagulation prior to the membranes is not necessary in all cases (Pearce, 2007), but when beneficial, commonly the doses needed are clearly lower than those needed for conventional pre-treatment (Fiksdal and Leiknes, 2006, Leiknes, 2009, Pearce, 2008), typically 40% or less (Pearce, 2008). As a result, micro-coagulation could be implemented in order to improve membrane performance during low turbidity events (see Chapter 4). A study based on TEPs effect on membrane fouling found out that that a significant improvement in fouling control was experimented when using in-line coagulation (Villacorte et al., 2009b).

Regardless raw water turbidity, membrane resistance fluctuated along time. After a CEB, resistance increased over time and, despite the HC performed, it reached a maximum value and then decreased, not necessarily coinciding with a CEB (Figure 4.4). The dependency between resistance oscillation and other raw water physico-chemical parameters apart from turbidity (pH, conductivity, DOC, UV_{254}, etc.) was analysed but a clear relationship could not be established due to the large number of parameters changing simultaneously in natural waters. This fluctuation of resistance values may be explained by the synergisms of different feed water components interactions as claimed by Hong et al. (1997) and Seidel et al. (2002) for nanofiltration (NF) membranes, as well as membranes and raw water components interactions.

The membrane water yield was 78-87% at 15 and 30 min of filtration time respectively, and the chemical consumption (used in CEBs) per cubic meter of feed water was 0.7 mL NaOH/m^3, 2.8 mL NaClO/m^3 and 2.6 mL HCl/m^3.

3.3.2. Permeate quality

Despite the fluctuations of the feed water, the permeate produced presented a relatively constant quality in all the conditions tested, both at high and low turbidity events. Table 3.1 shows the results obtained until October 2011, highlighting the minimum, average and maximum values of each water quality parameter monitored.

As can be seen, turbidity and TSS were highly removed by the UF membrane (greater than 99% removal in both cases, on average), resulting into very low values independently of the raw water fluctuations. DOC was slightly removed by UF membrane (29% removal, on average) as well as UV_{254} (33% removal, on average). Nevertheless, DOC and UV_{254} removal were not goals to be achieved by a membrane based pre-treatment.

Microbiological parameters were completely removed by the considered UF membrane, except aerobic bacteria at 22ºC and filamentous algae. In the first case, despite the considerable reduction obtained, some colonies could be found in the permeate. This may be explained by their environmental presence, so that samples might have been infected by bacteria present in the atmosphere. In the case of filamentous algae, since their size are considerable larger than the membrane pore size (and membrane integrity was monitored monthly through pressure decay tests, not detecting any fibre broken), the most probable

explanation for their presence is that some colonies might exist in the permeate pipes or sampling point, so positive results were obtained and the permeate may be free of them.

Table 3.1. Raw and membrane permeate water quality limits (June 2011 - October 2011). LoQ: limit of quantification, MPN: Most-probable number, CFU: Colony forming units.

Parameter	Raw water			Permeate water		
	Min	Average	Max	Min	Average	Max
Turbidity (NTU)	20	171	>800	0.03	0.05	0.40
Total suspended solids (mg/L)	48.5	91.6	272.5	<LoQ	0.6	3.3
DOC (mg/L)	2.9	4.8	45.3	2.7	3.4	6.1
UV_{254} (cm^{-1})	0.069	0.112	0.471	0.064	0.075	0.097
SDI_{15} (%/min)	4.4	>5.0	>5.0	0.1	0.7	2.7
E. coli [log_{10} (MPN/100mL)]	2.82	3.30	4.66	Absence	Absence	Absence
Aerobic bacteria at 22ºC [log_{10} (CFC/mL)]	3.76	4.45	5.43	1.49	2.44	4.64
Clostridium perfringens [log_{10} (CFU/100mL)]	2.60	3.37	4.32	Absence	Absence	Absence
Total Coliforms [log_{10} (MPN/100mL)]	3.99	4.50	5.86	Absence	Absence	Absence
Faecal Coliforms [log_{10} (MPN/100mL)]	2.94	3.49	4.11	Absence	Absence	Absence
Filamentous algae [log_{10} (cells/mL)]	3.39	3.70	4.03	0.48	0.82	1.20

The fouling indicator SDI_{15} of permeate water was always within RO membrane manufacturers specifications (<3%/min). Therefore, despite the reported limitations of the SDI method (Alhadidi et al., 2011, Schippers and Verdow, 1980, Yiantsios and Karabelas, 2003), a subsequent RO could be successfully connected and thus, lead to a much more compact treatment for DWTPs.

3.4. Conclusions

This study shows that direct UF is a suitable alternative in technical terms to conventional DWTP pre-treatment (dioxichlorination, coagulation/flocculation, settling and sand filtration), especially for periods with high and extremely-high water turbidity. In this case, cake formation appears to be the main fouling mechanism, so that probably larger particles accumulate on the membrane surface and prevent small organic compounds, which are responsible for not physically removable fouling, reaching the membrane. Also the cake layer formed may be more porous and less tightly linked to the membrane. On the contrary, during low turbidity events, the cake layer formed may not be so significant, so that molecules susceptible of being adsorbed and/or deposited in/into the membrane may reach it and cause greater resistance build up. Additionally, the fouling accumulated may be linked more strongly than in higher turbidity periods, becoming more difficult to remove. This turns into the need to increase the cleaning operations frequency, especially the chemically enhanced ones. Further insights in this regard were included in Chapter 4, covering a wider period of time as well to better understand the membrane behaviour under different scenarios.

Water quality produced along the testing period remained nearly constant, so that UF proved to provide treated water independently of feed water characteristics, regardless of its large fluctuations. Most of the physico-chemical parameters assessed were removed to a larger extent by direct UF than by conventional pre-treatment and most of the microbiological indicators assessed (total coliforms, faecal coliforms, *E. coli* and *Clostridium perfringens*) were completely removed by direct UF in all the sampling campaigns. The fouling index SDI_{15} was below 3%/min all the time (with average values of 0.7), which is the recommended value for a subsequent RO process. Chapter 4 reported the water quality results of two years of continuous operation, in order to demonstrate the long term performance.

Direct UF proved to be an efficient pre-treatment for DWTPs capable of working continuously regardless of feed water quality fluctuations and of producing stable high quality permeate. Under the tested conditions, it presented a high water yield (78-87%) and a low chemical consumption (0.7 mL NaOH/m^3, 2.8mL NaClO/m^3 and 2.6 mL HCl/m^3), only associated to membranes cleaning and thus, avoiding chemical pre-treatment (dioxichlorination, coagulation / flocculation). The optimisation of direct UF was studied in Chapter 4, aiming at comparing its competitiveness with DWTPs current conventional pre-treatment.

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CHAPTER 4

Micro-coagulation effects on direct ultrafiltration of challenging raw river water

This chapter is based on:

Ferrer, O., Dekker, R., Mesa, J., Martín-Alonso, J., Cortina, J.L., Gibert, O., (under review) Micro-coagulation effects on direct ultrafiltration of challenging raw river water.

DOI:

Abstract

The direct UF treatment scheme proposed previously was assessed during two years under different scenarios. One full scale UF membrane module (nominal capacity: 5.0 m^3/h) was operated continuously treating challenging raw river water (turbidity: 5 - >1,000 NTU, DOC: 2 - 14 mgC/L, UV_{254}: 0.062 – 0.430 cm^{-1}), demonstrating the feasibility of substituting DWTPs conventional pre-treatment and optimising its performance under the different conditions faced. Summer periods enabled the attainment of higher filtration fluxes (70 L/(m^2·h) vs. 40 L/(m^2·h)), although raw river water showed greater fouling potential (SDI_{15}, $MFI_{0.45}$), turbidity and TSS content. Winter periods presented a higher DOC concentration, with greater biopolymers content, which have been claimed as main membrane foulants. When a preliminary micro-coagulation of $FeCl_3$ (<1.5 mg/L as Fe(III)) was performed, the achievable hydraulic conditions both in summer and in winter were harsher (70 L/(m^2·h) of filtration flux, 45 min of filtration time, 1 CEB/day and 96.7% and 94.7% of water yield in summer and winter, respectively), enabling the implementation of similar conditions along the year. Impacts on filtration were more pronounced in winter (specific cake resistance was lowered 6 fold and was significantly stabilised in winter), but a positive effect was also noticed in hydraulic and chemical cleaning stages, increasing the efficiency of the former and decreasing to half the frequency of the later.

4.1. Background

Freshwater scarcity has become a major concern in many arid and semi-arid countries worldwide to such an extent that meeting current and future water demand is one of the main challenges for mankind (UNESCO, 2009). Several factors have led to this water scarcity context, including increasing demand due to continued population growth and new consumption patterns, industrial development, dependence on single supply sources, depletion and pollution of groundwater as well as hydrological and climate changes, among others (Bixio et al., 2006, Verstraete et al., 2009, Miller, 2006). This requires the implementation of more efficient treatment schemes as well as processes capable of dealing with low quality resources. Low pressure membrane filtration has proved good removal capabilities which have led to a remarkable application within the water treatment scheme (Freeman et al., 2006). In drinking water treatment plants (DWTPs) dealing with surface water, ultrafiltration (UF) is typically implemented after a preliminary pre-treatment consisting of coagulation/flocculation, settling and granular media filtration, sometimes assisted by an initial disinfection. However, some works have addressed the possibility of raw river water direct UF as an alternative to conventional pre-treatment for DWTPs. The associated envisaged advantages would be a decrease in reagents dosage and thus of solid waste generation, low footprint, easiness to be implemented due to its modularity (Pearce, 2007) as well as a decrease in the capital and operational expenses of a subsequent reverse osmosis (RO) stage (Fritzmann et al., 2007). Initial experiences have been reported with successful results but in most cases these studies were performed during few days/months (Rojas et al., 2008, Xia et al. 2004, Vos et al., 1998) and/or with raw water of relatively stable quality (Hofman et al., 1998, Mierzwa et al., 2012, Rojas et al., 2008, Xia et al. 2004, Vos et al., 1998). As a consequence, their results cannot be extrapolated for full scale plants, which need to operate continuously, often with variable feed water. On the other hand, other works faced technical difficulties (Clever et al., 2000) or even concluded that direct UF was not suitable to treat raw river water without any pre-treatment (Li and Dong, 2008). Recently, Galvañ et al. (2014) and Briceño et al. (2014) have reported successful results at pilot scale after two years of operation. Due to the discrepancy of the conclusions drawn, together with the different conditions tested which difficult the comparison of the results, more research is needed to determine the feasibility of direct UF, to optimise its performance under different scenarios and finally to compare it with conventional pre-treatment.

A main limiting factor for a wider membrane filtration processes application is fouling (Huang et al., 2009). Indeed, fouling results in an increased transmembrane pressure (TMP) and thus, more frequent cleaning is required. This in turn can cause membrane deterioration and decrease the process water yield (ratio between net permeate produced and intaken water). As a result, it becomes necessary to determine the fouling impact on real scale applications, as well as to define strategies to minimise its negative effects. Precoagulation (with or without sedimentation) has been defined as the most successful pre-treatment to reduce fouling on low pressure membranes (Huang et al., 2009). However, when combining coagulation and UF, the conditions and doses applied are not the same as those used in conventional water treatment (Pearce, 2008), Fiksdal and Leiknes, 2006, Huang et al., 2009), being typically 40% or

less (Pearce, 2008). Studies on hybridizing precoagulation (with or without sedimentation) and UF can be found in the literature (Guigui et al., 2002, Sun et al., 2009, Lerch et al., 2005, Konieczny et al., 2006, Xiangli et al., 2008, Qin et al., 2006, Zheng et al., 2012). These studies targeted total organic carbon (TOC) removal because UF presents a limited capacity to retain it.

This work addressed the implementation and optimisation of direct UF treating highly variable raw river water, using a commercially available full scale module and operating continuously during two years. This represented an intensive testing to ensure the feasibility of the proposed alternative, from sanitary, technical, economic and environmental perspectives, paving the way for its future implementation in DWTPs. The effects of conducting a preliminary micro-coagulation were quantified in summer and winter periods, both at filtration and cleaning stages. Coagulant was dosed at micro-scale, just aiming at improving the subsequent filtration stage, which differed from the abovementioned studies. In addition to this, due to the duration of the study, seasonal differences when coupling coagulation/UF were taken into account in a highly variable water source, complementing those studies as well. The conventional fouling mechanisms laws were considered, in order to identify whereas a different blocking law applied in each case, and thus, could explain the differences encountered.

4.2. Materials and methods

4.2.1. Experimental set up

The experimental set up consisted of a prototype plant equipped with a strainer (300 μm) followed by a pressurised inside-out UF membrane system (Pentair X-Flow Aquaflex module, dead end mode, polyethersulfone (PES), 20 nm pore size) automatically controlled by a supervisory control and data acquisition (SCADA) system (Figure 4.1). The prototype worked at constant permeate flow and had a nominal capacity of 5.0 m^3/h. It filtered Llobregat raw river water directly and continuously during 2 years (May 2011 – April 2013). The filtration process was automatically stopped when a pre-set value of either TMP (1 bar) or hydraulic resistance ($1E^{+13}m^{-1}$) was reached. More details about the experimental set up can be found in a previous work (Ferrer et al., 2013b). The prototype plant was installed in Sant Joan Despí DWTP (Barcelona metropolitan area, Spain) and its performance was compared to its current pre-treatment, consisting of dioxichlorination, coagulation/flocculation, settling and sand filtration. The Llobregat River presents a typical Mediterranean behaviour, experiencing large flow fluctuations (severe droughts during summer and flash flood events in spring and autumn) with its associated water quality variations, and also suffers from historical industrial and urban contamination (Hutzinger, 2012). This provides a challenging scenario to conduct feasibility studies of water treatment technologies.

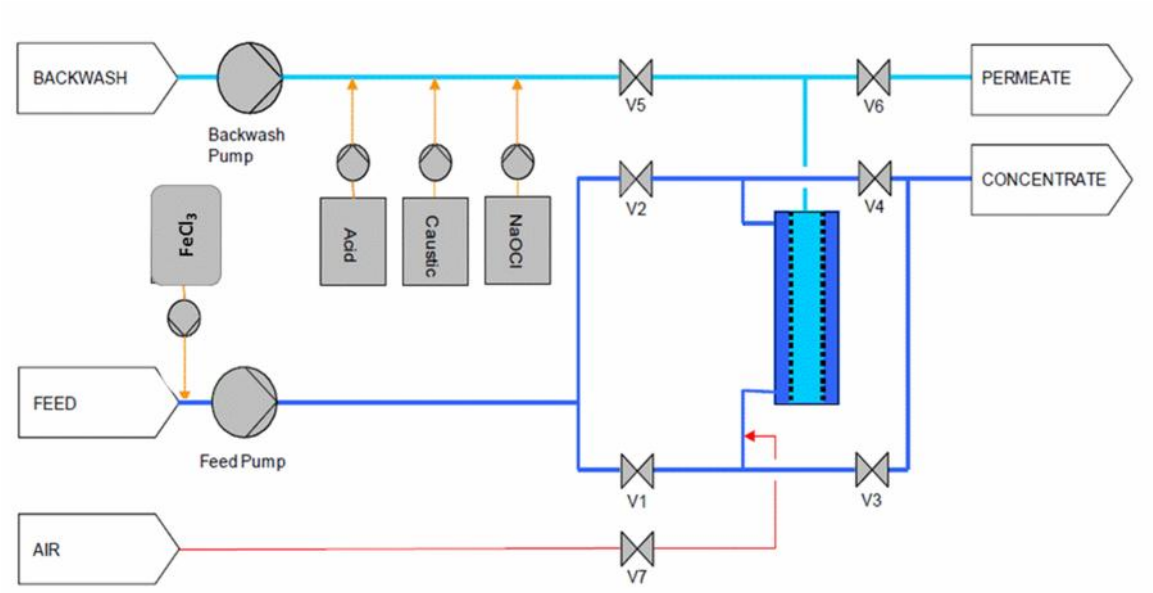

Figure 4.1. Prototype plant sketch, where the main streams, pumps, reagents, valves and the membrane module have been represented.

During the whole 2 year period studied the hydraulic cleaning (HC) and the chemically enhanced backwash (CEB) sequences were not modified. The HC involved a forward flush of 62.5 L/(m^2·h) for 20 s, a UF permeate backwash flux of 250 L/(m^2·h) for 20 s enhanced by an airflush of 10 Nm^3/h for 10 s and a final forward flush of 62.5 L/(m^2·h) for 40 s. The CEB was composed of a basic-oxidising stage (NaOH [49/50%, Severn Trend, Spain] and NaClO [Severn Trend, Spain] dosing) and an acid stage (HCl [15%, Severn Trend, Spain] dosing) subsequently. The CEB sequence consisted in an HC, a basic-oxidising dosing (125 L/(m^2·h), 45 s), a soaking with those chemicals (10 min), a rinsing (250 L/(m^2·h), 45 s), an acid dosing (125 L/(m^2·h), 45 s), a soaking with that chemical (10 min) and a rinsing (250 L/(m^2·h), 45 s) stage. Alkaline solution (NaOH) concentration was 480 mg/L, oxidiser (NaClO) 200 mg/L and acid (HCl) 438 mg/L.

Non-coagulation and coagulation periods were tested, in order to assess the differences in hydraulic behaviour of the UF membrane. In the latter case, an in-line micro-coagulation was conducted just before the feed pumping system (so that the turbulence created by the pump ensured the adequacy of the hydraulic conditions). It was termed as micro-coagulation because the doses applied (< 1.5 mg/L Fe(III)) were well below those required for conventional coagulation purposes (20 – 35 mg/L of Fe(III) according to (Edzwald, 2011) for pH 8.0 (raw river water average) and dissolved organic carbon (DOC) content of 4.4 and 7.3 mg C/L (summer and winter respectively)). The aim of the micro-coagulation hence, was to aid filtration rather than decreasing the DOC content. The micro-coagulation dose was controlled by a dynamic Smart Control system (ViCA software) developed by Pentair. More details can be found in (Blankert et al., 2007) but basically this system adjusted the coagulant dose based on the hydraulic resistance trend after each HC. The coagulant tested was ferric chloride (40%, Severn Trent, Spain).

4.2.2. Water quality characterisation

Both Llobregat River water and membrane permeate stream were analysed on a periodical basis. The parameters monitored and the methods used were: temperature by resistivity (Endress & Hausser TR10-ABG1HD-SAG2000), conductivity by electrometry (Endress & Hausser CLS21D-C1+CM42-KAA000EAN00), pH by potenciometry (Hach-Lange DPD1P.99), turbidity by nephelometry (Hach-Lange Ultraturb SC), total suspended solids (TSS) by ESS 340.2, absorbance at 254nm (UV_{254}) by spectrophotometry (Hach-Lange DR 5000), silt density index (SDI_{15}) and modified fouling index ($MFI_{0.45}$) by ASTM D4189 (Simple SDI Meter 9C-281-0157), DOC by combustion-infrared method using a DOC analyser (non-purgeable organic carbon, UNE-EN 1484), after filtration with a 1.2 µm glass fibre filter for the raw water samples (TOC-V CSH Shimadzu), particle size distribution by laser beam extinction (HIAC Royco, Pacific Scientific), total coliforms, faecal coliforms and *E. coli* quantification by the defined substract method (most probable number) and *Clostridium perfringens* and aerobic bacteria at 22˚C by plate counting.

Fractionation of DOC was performed by HPSEC using a Toyopearl TSK HW-50S column (250x20 mm) coupled to on-line UV_{254}, organic carbon and organic nitrogen detectors by DOC-Labor (Karlsruhe) as described in (Huber et al., 2011). The main fractions obtained by these analyses were the non-chromatographic (HOC), and the chromatographic one, which in turn was classified into a) biopolymers (BP) (molecular weight (MW) >20000 g/mol, basically constituted by polysaccharides and proteins); b) humic substances (HS) (MW of approx. 1000 g/mol, constituted by fulvic and humic acids); c) building blocks (BB) (MW between 300 and 500 g/mol, constituted by breakdown products of humics); d) low molecular weight acids (LMWA) (MW<350 g/mol, constituted by alcohols, aldehydes, ketones, sugars and amino acids); e) low molecular neutrals (LMWN) (MW<350 g/mol, constituted by alcohols, aldehydes, ketones and amino acids).

Airflow tests were conducted at least once a month to verify the membrane integrity, following the membrane manufacturer protocol. The membrane module was drained, the valves surrounding the membrane housing were closed, the membrane feed side was pressurised at 1 bar during 5 min and a valve on the permeate side was opened. The air flow passing through that valve was continuously registered. If the airflow was greater than 0.2 Nm^3/h, it indicated that the membrane had been compromised, since air was not only diffusing through the membranes, but also passing through broken fibres.

4.2.3. Calculations and data treatment

Hydraulic resistance (R) (m^{-1}), which accounted for the membrane resistance itself as well as the resistance offered by the accumulated foulants, was used to characterise the UF membrane hydraulic performance, calculated by the Darcy equation. HC cleaning efficiency (dimensionless) was calculated as shown in Eq. 4.1, and CEB cleaning efficiency (dimensionless) by Eq. 4.2, where $6E^{+11}$ m^{-1} was taken as virgin membrane resistance.

$$HC\ efficiency = \frac{Resistance\ after\ HC}{Resistance\ after\ the\ last\ CEB} \qquad \text{Eq. 4.1}$$

$$CEB\ efficiency = \frac{Resistance\ after\ CEB}{Virgin\ membrane\ resistance} \qquad \text{Eq. 4.2}$$

Specific cake resistance (α) (m^{-2}), which represents the increase of the cake layer resistance build up, was calculated by Eq. 4.3, where v is the specific volume (m^3/m^2) that is the filtered volume (V) (m^3) per unit area, A is the membrane surface area (55 m^2), J is the water flux ($m^3/(m^2 \cdot s)$) and t is the time (s).

$$\alpha = \frac{dR}{dv} = \frac{dR}{d\left(\frac{V}{A}\right)} = \frac{1}{J} \cdot \left(\frac{dR}{dt}\right) \qquad \text{Eq. 4.3}$$

Due to the high frequency of data acquisition within the prototype plant as well as the duration of the experiments (2 years), large amount of data was obtained. Consequently, an Excel (Microsoft) macro reducing it while keeping its representativeness was applied. One month physico-chemical, microbiological and operational parameters were considered for the comparison between winter / summer, coagulation / no coagulation periods, representative of each condition considered. Confidence intervals of 95% were used to provide information on the variability of values, and significance of 0.05 was applied to calculate differences among data sets (by means of Mintab).

4.3. Results and discussion

4.3.1. Direct ultrafiltration feasibility

The continuous operation of the direct UF scheme for 2 years demonstrated the feasibility of this configuration as an alternative to conventional drinking water pre-treatment processes (dioxichlorination, coagulation/flocculation, settling and sand filtration). The configuration proposed was able to continuously treat raw river water, independently of its fluctuations (e.g. turbidity ranging from 5 up to > 1000 NTU as shown in Figure 1.5, DOC between 2 – 14 mg C/L as depicted in Figure 1.6 and UV_{254} from 0.062 to 0.430 cm^{-1} as plotted in Figure 1.8) delivering product water of constant quality, equal or superior to the conventionally pre-treated one for most of the parameters monitored (Table 4.1, Figure 4.2). In particular, turbidity (0.068±0.004 vs. 0.313±0.031 NTU), TSS (0.92±0.17 vs. 1.03±0.16 mg/L), SDI_{15} (1.90±0.15 vs. 5.20±0.13 %/min), $MFI_{0.45}$ (0.85±0.73 vs. 25.18±11.35 L/s^2) and the microbiological parameters considered presented lower concentrations in the direct UF permeate, being significantly different the turbidity, SDI_{15} and $MFI_{0.45}$. Microbiological parameters assessed were consistently absent in the UF permeate, except for the aerobic bacteria at 22ºC, whose positive results could be due to their presence in the environment rather than for their passage through the membrane. Concentrations up to 6.2 $\log_{10}$ (MPN/100 mL) of total coliforms, 5.38 $\log_{10}$ (MPN/100 mL) of faecal coliforms, 5.20 $\log_{10}$ (MPN/100 mL) of *E. coli* and 4.96 $\log_{10}$ (MPN/100 mL) of *Clostridis perfringens,* which were the maximum values quantified in the raw river water, were completely removed by the direct UF scheme.

On the other hand, the DOC and the UV_{254} were removed to a larger extent by the conventional pre-treatment, being their values (3.77±0.16 vs. 3.51±0.19 mg/L and 0.0815±0.0018 vs. 0.0725±0.0028, respectively) significantly lower in the case of UV_{254}. In general, less variability was presented in the direct UF scheme, leading to a more stable process in all the conditions considered.

Table 4.1. Physico-chemical and microbiological results obtained of the raw river and the direct UF permeate in the four scenarios considered, as well as from conventionally pre-treated water (dioxichlorination, coagulation/flocculation, settling and sand filtration) for summer and winter periods. MPN: most probable number; CFU: colony forming unit; LoQ: limit of quantification.

Scenario	Parameter	Units	Sampling point	Minimum	Maximum	Average	St. deviation
No coag – Summer	Turbidity	NTU	Feed	35.4	186.0	63.9	32.9
			Permeate	0.038	0.148	0.068	0.027
	TSS	mg/L	Feed	< LoQ	232.0	76.8	58.0
			Permeate	< LoQ	1.75	1.05	0.65
	Temperature	ºC	Feed	20.8	30.4	26.4	1.9
	pH		Feed	6.99	8.80	8.09	0.40
	DOC	mg C/L	Feed	3.27	6.42	4.72	1.15
			Permeate	3.19	6.51	4.11	1.37
	UV_{254}	cm^{-1}	Feed	0.076	0.158	0.095	0.018
			Permeate	0.070	0.141	0.084	0.017
	SUVA	L/(cm·mg)	Feed	1.51	2.68	2.27	0.40
			Permeate	2.17	2.96	2.35	0.34
	SDI_{15}	(%/min)	Feed	> 6	> 6	> 6	N.A.
			Permeate	1.67	2.63	2.17	0.28
	$MFI_{0.45}$	L/s^2	Feed	898.0	5737.0	2686.3	2242.0
			Permeate	0.22	0.41	0.30	0.06
	Log_{10} (total coliforms)	Log_{10} (MPN/100mL)	Feed	3.89	5.86	4.56	0.77
			Permeate	*absence*	*absence*	*absence*	N.A.
	Log_{10} (faecal coliforms)	Log_{10} (MPN/100mL)	Feed	2.76	5.38	3.64	1.02
			Permeate	*absence*	*absence*	*absence*	N.A.
	Log_{10} (*E. coli*)	Log_{10} (MPN/100mL)	Feed	2.46	5.20	3.33	1.10
			Permeate	*absence*	*absence*	*absence*	N.A.
	Log_{10} (*Clostridium perfringens*)	Log_{10} (CFU/100 mL)	Feed	3.11	4.20	3.47	0.48
			Permeate	*absence*	*absence*	*absence*	N.A.
	Log_{10} (aerobic bacteria at 22ºC)	Log_{10} (CFU/mL)	Feed	3.85	4.95	4.27	0.51
			Permeate	0.30	5.65	2.83	2.20
No coag – Winter	Turbidity	NTU	Feed	4.6	53.0	24.3	15.4
			Permeate	0.052	0.097	0.074	0.014
	TSS	mg/L	Feed	4.0	51.5	24.4	16.8
			Permeate	< LoQ	1.00	0.31	0.47
	Temperature	ºC	Feed	4.8	14.0	9.2	2.1
	pH		Feed	6.59	8.93	8.15	0.28
	DOC	mg C/L	Feed	3.36	12.13	7.53	4.40
			Permeate	2.81	3.09	2.98	0.15
	UV_{254}	cm^{-1}	Feed	0.074	0.373	0.111	0.077
			Permeate	0.068	0.097	0.076	0.007
	SUVA	L/(cm·mg)	Feed	0.91	2.41	1.47	0.82

			Permeate	2.22	2.79	2.48	0.28
	SDI_{15}	(%/min)	Feed	> 6	> 6	> 6	N.A.
			Permeate	0.91	2.44	1.87	0.56
	$MFI_{0.45}$	L/s^2	Feed	87.1	589.3	415.9	284.9
			Permeate	0.07	0.26	0.17	0.07
	Log_{10} (total coliforms)	Log_{10} (MPN/100mL)	Feed	4.18	4.84	4.47	0.34
			Permeate	*absence*	*absence*	*absence*	N.A.
	Log_{10} (faecal coliforms)	Log_{10} (MPN/100mL)	Feed	3.94	4.30	4.13	0.18
			Permeate	*absence*	*absence*	*absence*	N.A.
	Log_{10} (*E. coli*)	Log_{10} (MPN/100mL)	Feed	3.23	3.52	3.35	0.15
			Permeate	*absence*	*absence*	*absence*	N.A.
	Log_{10} (*Clostridium perfringens*)	Log_{10} (CFU/100 mL)	Feed	3.00	3.11	3.06	0.06
			Permeate	*absence*	*absence*	*absence*	N.A.
	Log_{10} (aerobic bacteria at 22ºC)	Log (CFU/mL)	Feed	3.96	4.48	4.17	0.27
			Permeate	2.18	2.99	2.70	0.45
$FeCl_3$ – Summer	Turbidity	NTU	Feed	56.1	3140.0	262.8	635.4
			Permeate	0.034	0.126	0.048	0.021
	TSS	mg/L	Feed	58.0	3309.0	401.4	887.4
			Permeate	< LoQ	2.00	0.65	0.78
	Temperature	ºC	Feed	18.7	30.5	26.5	2.3
	pH		Feed	7.03	8.43	7.71	0.29
	DOC	mg C/L	Feed	2.87	7.01	4.13	1.78
			Permeate	2.48	4.19	3.20	0.81
	UV_{254}	cm^{-1}	Feed	0.061	0.159	0.084	0.031
			Permeate	0.051	0.128	0.068	0.022
	SUVA	L/(cm·mg)	Feed	2.12	2.26	2.18	0.05
			Permeate	1.84	2.27	2.01	0.17
	SDI_{15}	(%/min)	Feed	> 6	> 6	> 6	N.A.
			Permeate	1.67	3.67	2.74	0.80
	$MFI_{0.45}$	L/s^2	Feed	1088.0	20216.6	5109.2	8447.4
			Permeate	0.12	1.14	0.49	0.35
	Log_{10} (total coliforms)	Log_{10} (MPN/100mL)	Feed	4.21	5.86	4.77	0.68
			Permeate	*absence*	*absence*	*absence*	N.A.
	Log_{10} (faecal coliforms)	Log_{10} (MPN/100mL)	Feed	3.15	5.38	3.88	0.89
			Permeate	*absence*	*absence*	*absence*	N.A.
	Log_{10} (*E. coli*)	Log_{10} (MPN/100mL)	Feed	2.58	5.20	3.35	1.08
			Permeate	*absence*	*absence*	*absence*	N.A.
	Log_{10} (*Clostridium perfringens*)	Log_{10} (CFU/100 mL)	Feed	3.11	4.20	3.60	0.45
			Permeate	*absence*	*absence*	*absence*	N.A.
	Log_{10} (aerobic bacteria at 22ºC)	Log_{10} (CFU/mL)	Feed	3.85	4.95	4.29	0.45
			Permeate	0.60	1.78	1.19	0.83
$FeCl_3$ – Winter	Turbidity	NTU	Feed	5.3	74.1	19.2	16.5
			Permeate	0.059	0.193	0.081	0.030
	TSS	mg/L	Feed	< LoQ	96.5	22.4	27.2
			Permeate	0.25	1.00	0.50	0.35
	Temperature	ºC	Feed	5.5	17.9	8.6	1.6
	pH		Feed	6.98	8.59	7.77	0.34
	DOC	mg C/L	Feed	3.10	16.13	7.08	6.10
			Permeate	3.24	4.22	3.63	0.44
	UV_{254}	cm^{-1}	Feed	0.061	0.157	0.091	0.023
			Permeate	0.061	0.087	0.077	0.007

	SUVA	L/(cm·mg)	Feed	0.92	2.22	1.75	0.59
			Permeate	2.01	2.41	2.22	0.18
	SDI_{15}	(%/min)	Feed	> 6	> 6	> 6	N.A.
			Permeate	1.87	2.80	2.42	0.30
	$MFI_{0.45}$	L/s^2	Feed	263.4	3003.7	859.8	1199.2
			Permeate	0.18	0.88	0.47	0.23
	Log_{10} (total coliforms)	Log_{10} (MPN/100mL)	Feed	5.43	5.64	5.54	0.15
			Permeate	*absence*	*absence*	*absence*	N.A.
	Log_{10} (faecal coliforms)	Log_{10} (MPN/100mL)	Feed	5.04	5.30	5.17	0.18
			Permeate	*absence*	*absence*	*absence*	N.A.
	Log_{10} (*E. coli*)	Log_{10} (MPN/100mL)	Feed	4.38	5.04	4.71	0.47
			Permeate	*absence*	*absence*	*absence*	N.A.
	Log_{10} (*Clostridium perfringens*)	Log_{10} (CFU/100 mL)	Feed	4.08	4.08	4.08	N.A.
			Permeate	*absence*	*absence*	*absence*	N.A.
	Log_{10} (aerobic bacteria at 22ºC)	Log_{10} (CFU/mL)	Feed	4.94	4.94	4.94	N.A.
			Permeate	1.18	1.18	1.18	N.A.
Sand filters – Winter	Turbidity	NTU	Permeate	0.198	0.469	0.321	0.086
	TSS	mg/L	Permeate	< LoQ	1.50	0.50	0.87
	Temperature	ºC	Permeate	5.7	16.8	9.4	4.0
	pH		Permeate	7.75	8.86	8.30	0.38
	DOC	mg C/L	Permeate	2.85	6.24	4.55	2.39
	UV_{254}	cm^{-1}	Permeate	0.058	0.076	0.065	0.0056
	SUVA	L/(cm·mg)	Permeate	0.98	2.38	1.68	0.99
	SDI_{15}	(%/min)	Permeate	4.52	5.42	4.98	0.34
	$MFI_{0.45}$	L/s^2	Permeate	3.80	23.93	8.69	8.59
	Log_{10} (total coliforms)	Log_{10} (MPN/100mL)	Permeate	0.48	1.43	0.75	0.46
	Log_{10} (faecal coliforms)	Log_{10} (MPN/100mL)	Permeate	*absence*	0.60	0.30	0.43
	Log_{10} (*E. coli*)	Log_{10} (MPN/100mL)	Permeate	*absence*	0.60	0.30	0.43
	Log_{10} (*Clostridium perfringens*)	Log_{10} (CFU/100 mL)	Permeate	0.60	1.08	0.90	0.21
	Log_{10} (aerobic bacteria at 22ºC)	Log_{10} (CFU/mL)	Permeate	2.08	2.76	2.46	0.30
Sand filters – Summer	Turbidity	NTU	Permeate	0.129	0.435	0.254	0.111
	TSS	mg/L	Permeate	1.25	2.00	1.65	0.285
	Temperature	ºC	Permeate	22.5	29.4	25.9	2.6
	pH		Permeate	7.88	8.75	8.32	0.33
	DOC	mg C/L	Permeate	2.65	3.86	3.38	0.502
	UV_{254}	cm^{-1}	Permeate	0.053	0.080	0.067	0.009
	SUVA	L/(cm·mg)	Permeate	1.97	2.28	2.13	0.13
	SDI_{15}	(%/min)	Permeate	4.97	6.21	5.56	0.45
	$MFI_{0.45}$	L/s^2	Permeate	4.07	41.70	10.89	11.00
	Log_{10} (total coliforms)	Log_{10} (MPN/100mL)	Permeate	3.99	6.41	5.01	1.01
	Log_{10} (faecal coliforms)	Log_{10} (MPN/100mL)	Permeate	*absence*	2.20	0.72	1.02
	Log_{10} (*E. coli*)	Log_{10} (MPN/100mL)	Permeate	*absence*	2.08	0.77	0.87
	Log_{10}	Log_{10}	Permeate	*absence*	1.79	0.50	0.78

	(*Clostridium perfringens*)	(CFU/100 mL)					
	Log_{10} (aerobic bacteria at 22ºC)	Log_{10} (CFU/mL)	Permeate	2.66	3.96	4.49	0.60

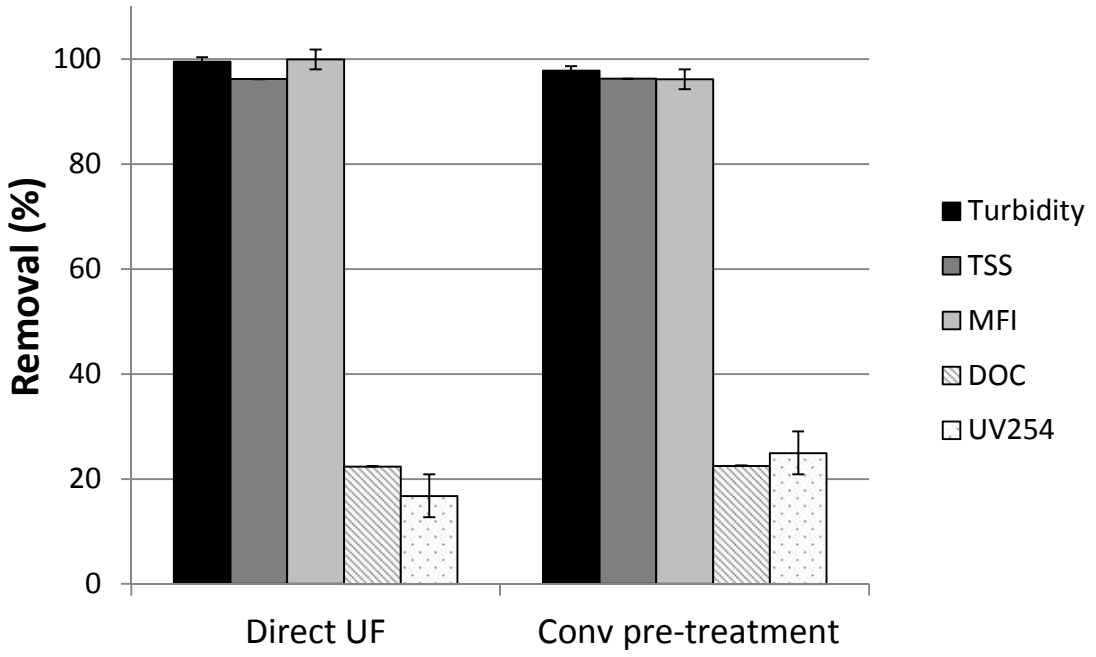

Figure 4.2. Removal percentage of various physico-chemical parameters by the direct UF and the conventional pre-treatment schemes. SDI_{15} removal could not be calculated because raw river water SDI_{15} values were above high level (> 5%/min). Error bars correspond to the standard error (number of samples: 347 for turbidity, 118 for TSS, 100 for $MFI_{0.45}$, 70 for DOC, and 350 for UV_{254}).

Airflow tests as well as membrane integrity tests with virus surrogates following the procedure described in Ferrer et al. (2013a) were periodically carried out (every 1 and 3 months respectively). They both indicated that the membrane integrity had not been compromised, because the airflow registered (0.051 ± 0.006 Nm^3/h) during the airflow integrity tests was well below the threshold defined by the membrane manufacturer as indicative of a breach (0.2 Nm^3/h) and there was not an increase of microbes passage in the tailored tests performed along time (data not shown).

It was not possible to determine by multi-variant analyses clear relationships between the hydraulic resistance evolution and several physico-chemical feed water parameters, such as turbidity, pH, conductivity, temperature, water viscosity, as well as operational parameters, such as HC frequency, filtration time, etc. An empirical model capable of predicting the hydraulic resistance behaviour based on the collected data could not be defined. The difficulties encountered in the modelling study suggested a set of processes occurring, turning into a complex system probably aggravated by the challenging raw river water tested. Despite

the impossibility of obtaining a reliable model describing and predicting the hydraulic resistance evolution, the influence of physico-chemical parameters on the UF performance was studied in detail.

Optimal operational conditions aiming at maximising the water yield and the filtration flux maintaining the UF TMP below 1 bar and the resistance below $1E^{+13}$ m^{-1} were established (Table 4.2). The highest water yields achieved ranged between 94.0% - 94.7% in optimal conditions, involving one or two CEBs per day, TMP below 1 bar and filtration fluxes of 40 – 70 $L/(m^2 \cdot h)$. Reagents consumption per cubic meter of feed water was 0.6 – 2.1 mL $NaOH/m^3$, 1.2 – 4.3 mL $NaClO/m^3$, 2.5 – 8.6 mL HCl/m^3 (CEBs) and 0 – 1.5 mg Fe^{3+}/L (micro-coagulation). These values were competitive with the current conventional pre-treatment, since water losses of the latter accounted for 5% and the chemical consumption for 32.2 mg PAX-18/L and 2 mg ClO_2/L for the considered period. Consequently, the waste generation would be greater in the conventional pre-treatment scheme. Finally, the direct UF scenario enabled the treatment of raw river water regardless of its quality. The conventional pre-treatment was typically stopped when turbidity was above 500 - 1000 NTU to avoid destabilising the system, whereas the direct UF scheme enabled the continuous operation, even for values greater than 1000 NTU.

Table 4.2. Optimal operational conditions defined during the 2 year operation.

Season	**Summer**		**Winter**	
Micro-coagulation applied?	No	Yes	No	Yes
Filtration flux ($L/(m^2 \cdot h)$)	70	70	40	70
Filtration duration (min)	45	45	120	45
TMP range (bar)	0.16 – 0.73	0.14 – 0.97	0.13 – 0.62	0.35 – 0.79
CEB frequency (# CEB/day)	2	1	2	1
Water yield (%)	94.0	94.7	94.5	94.7

As can be seen in Table 4.2, the UF behaviour differed between winter and summer, as well as when micro-coagulation was applied. These differences could be due to the membrane itself (e.g. polymer properties) and the water characteristics (e.g. temperature, natural organic matter (NOM) content and composition, inorganic compounds concentration).

In general, during summer periods greater filtration fluxes could be applied in a sustainable way. However, the lower filtration flux achievable in winter could be counterbalanced by a longer filtration time, leading to a similar water yield. The higher attainable filtration fluxes could be due to the hotter temperatures from summer, involving lower water viscosity and thus, lower TMP for a given flux. Nevertheless, seasonal differences in fouling nature and content, encompassed within the hydraulic resistance term, could also contribute to this behaviour. Table 4.1 summarises the water quality of both the UF feed stream (raw river water) and the UF permeate produced during one month in each of the situations studied. Despite the variability of the Llobregat River, the temperature (26.5 vs. 8.9ºC), turbidity (163.4±144.1 vs. 21.8±5.4 NTU), TSS (239.1±265.3 vs. 23.4±10.4 mg/L), SUVA (2.2±0.2 vs. 1.8±0.5 L/(cm·mg)) and $MFI_{0.45}$ (3897.8±3697.0 vs. 637.9±656.6 s/L^2) tended to be higher in summer than in winter, whereas the DOC, lower (4.4±0.8 vs. 7.3±3.7 mg C/L). Particle size

distribution showed a larger particle content in summer than in winter (449421±19953 vs. 150777±55969 particle/mL), which is in accordance with greater TSS content. Nevertheless, the percentage of smaller particles was higher in winter. Some of the parameters mentioned have been reported to impact membrane performance, which may explain the seasonal differences encountered. Low temperatures (6.5 – 11ºC) have been reported to accelerate irreversible fouling (Ma et al., 2013). Cakes formed by smaller particles (whose percentage was higher in winter) are more compact and less porous (Sripui et al., 2011), presenting a greater resistance, according to Carman-Kozeny equation. DOC content has been identified as the most detrimental component in terms of fouling when filtering surface water (Zularisam et al., 2006) and its concentration was higher in winter. In particular, DOC fractionation results (Figure 4.3) showed a higher biopolymers (BPs) concentration in winter compared to summer time. This could partially explain the seasonal differences experienced in membrane filtration performance, since BPs have been described as main membrane foulants (Neubrand et al., 2010).

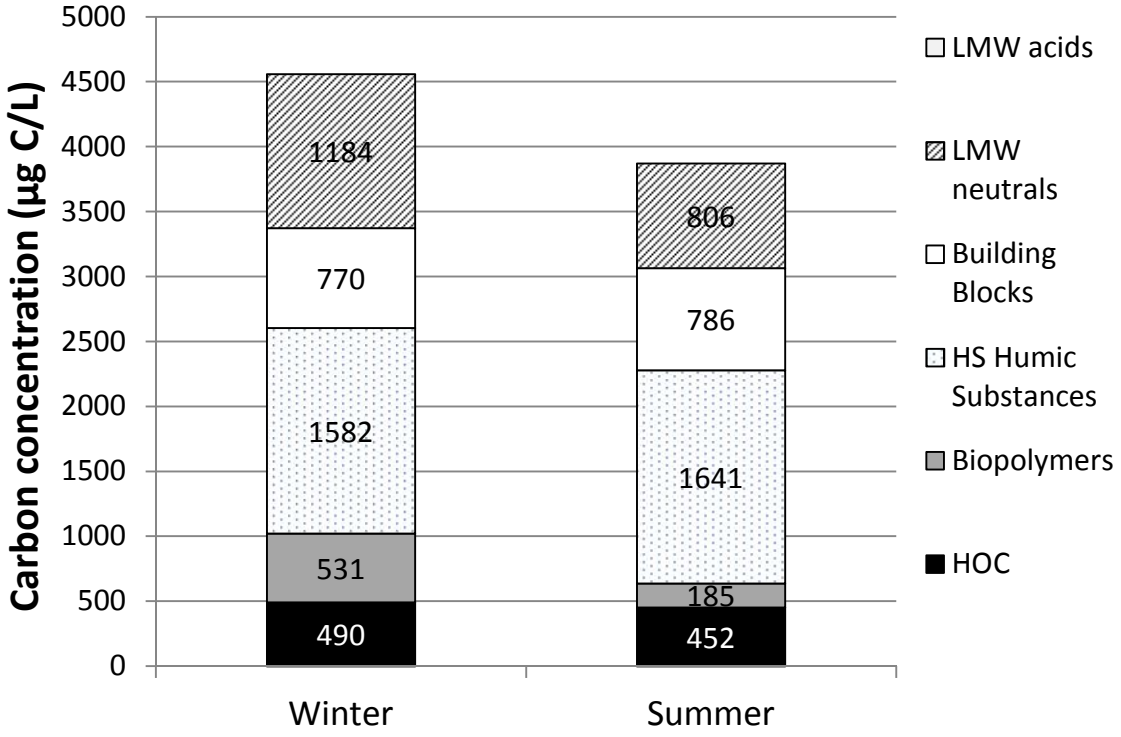

Figure 4.3. Raw river water DOC fractionation in winter and summer time. Numbers in the boxes indicate the concentration of each fraction in µg C/L.

Despite SDI and MFI are used to assess the fouling potential in RO membranes and SDI is intended for water samples whose turbidity is below 1 NTU (American Society for Testing and Materials (ASTM) SDI 4189-07 procedure) it could be questioned if these parameters could also provide insights into the fouling propensity of an UF membranes. Within this study, higher fouling index values (SDI_{15} and $MFI_{0.45}$) were encountered in raw river water during summer periods, which would suggest larger UF membrane fouling. However, the hydraulic resistance increase rate was higher in winter (see section 4.3.2.i) and thus, the assessed membrane was

able to sustain higher filtration fluxes in summer, suggesting that SDI_{15} and $MFI_{0.45}$ could not be used for such purpose. Some limitations of both indexes are already reported in literature when used as indicators of RO fouling propensity (Al-hadidi, 2011, Rachman et al., 2013, Koo et al., 2013, Salinas Rodríguez, 2011). For instance, SDI is not corrected for variations in pressure, temperature and pore size and membrane resistance of the used filter. In the case of MFI, results show a pressure dependency due to cake compression when measured at constant pressure, very high initial fluxes are attained initially, not representative of a RO system.

A micro-coagulation step prior the UF unit had a positive impact on the filtration fluxes attainable in winter (40 L/(m^2·h) vs. 70 L/(m^2·h)). The enhancement of membrane filtration hydraulic performance due to a precoagulation (with and without settling) has been reported formerly (Blankert et al., 2007, Choi and Dempsey, 2004, Doyen et al., 2003, Fan et al., 2008, Huang et al., 2009, Kabsch-Korbutowicz, 2006, Neubrand et al., 2010, Wang and Wang, 2006, Zheng et al., 2012). This might be due to the formation of a protective cake which prevents some compounds depositing into/onto the membrane or lead to a more porous cake which results into less resistance gain over the filtration cycle as stated elsewhere (Blankert et al., 2007). Also, iron salts based coagulants have been noted to remove BPs and humic acids (Neubrand et al., 2010, Zheng et al., 2012), reducing the foulants load and hence, improving the hydraulic membrane performance. Because the coagulant doses used were low, not targeting a DOC decrease, the contribution in this regard may be limited.

The micro-coagulation also reduced seasonal effects on the UF performance. Indeed, when micro-coagulation was applied, the attainable filtration flux and duration in both seasons were more similar. Doyen et al. (2003) reported similar benefits, as well as the possibility of extending the cleaning frequency, which was also experienced within this work (Table 4.2). From an engineering standpoint, a design enabling the implementation of the same filtration flux through the whole year would be preferred, as well as those conditions maximising filtration flux since this would require lower membrane surface area.

Despite some previous works have experienced an increase in the permeate quality when undertaking a preliminary coagulation step (with and without settling) (Konieczny et al., 2006, Konieczny et al., 2009, Shon et al., 2004, Xia et al., 2007), no significant differences were encountered in this work for most of the monitored parameters, as can be seen in Table 4.1. Nevertheless, the doses applied in the abovementioned experiments were higher than the ones used within this study (< 1.5 mg Fe(III)/L). Actually, Kim et al. (2005) observed that increased removals of TOC and UV_{254} occurred above a certain coagulant dose (10 mg/L of alum in his study). Other authors have reported a non-increase in UF permeate quality when applying a preliminary coagulation (Fan et al., 2008, Xiangli et al., 2008).

Only SDI_{15} and $MFI_{0.45}$ presented different (greater) values in the UF permeate when a micro-coagulation was performed, which could be due to the dissolved fraction of iron(III) able to pass the membrane.

4.3.2. Micro-coagulation effects on UF membrane performance

The positive effect of conducting a micro-coagulation prior to the UF on bearable hydraulic conditions was studied from a filtration and a cleaning standpoint, in order to identify the origin of the impact. For such purpose, one month period data was analysed under the four scenarios addressed (summer/winter, coagulation/no coagulation), at 70 L/(m^2·h) filtration flux, except for the winter - no coagulation scenario where the maximum sustainable filtration flux achieved was 40 L/(m^2·h).

<u>i) Coagulant effect on hydraulic resistance evolution during filtration cycles</u>

Figure 4.4 and Figure 4.5 represent the hydraulic resistance (black symbols), the feed water turbidity (dark grey symbols) and the coagulant dose (pale grey symbols) evolution along time in summer and winter, respectively. CEB performance is indicated as well (open circles) to better understand the membrane behaviour.

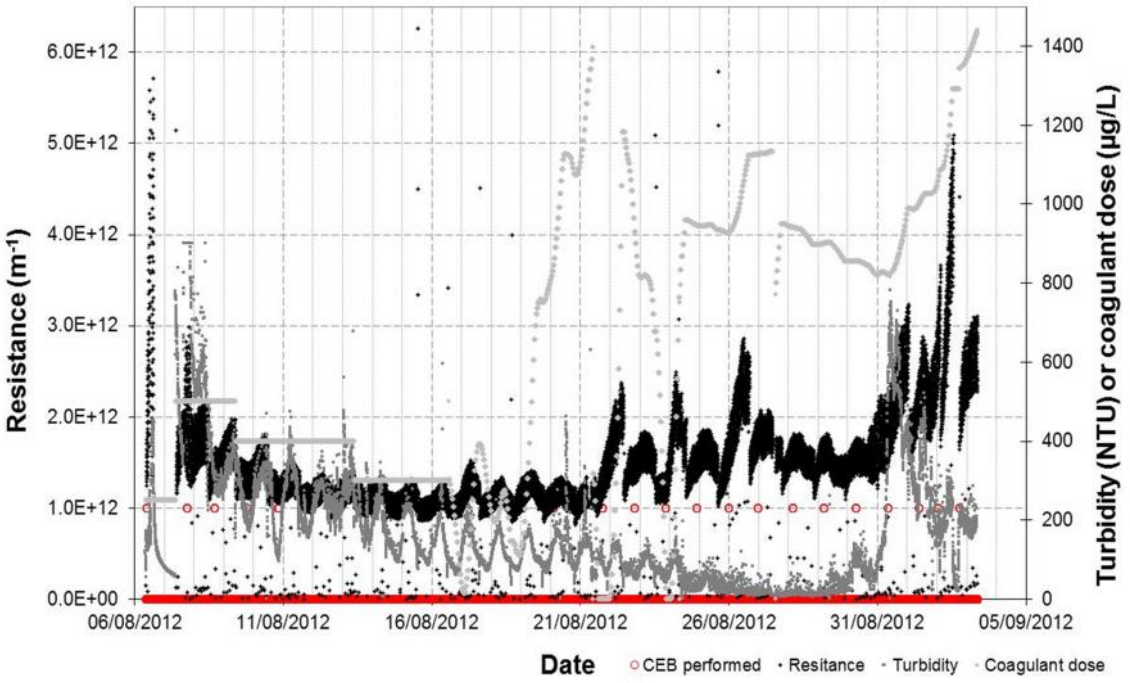

Figure 4.4. Hydraulic resistance (black symbols), feed water turbidity (dark grey symbols) and coagulant dose (pale grey symbols) evolution along time in summer conditions. Open circles, arbitrarily marked at $1E^{+12}$ m^{-1}, correspond to the moment when a CEB was performed.

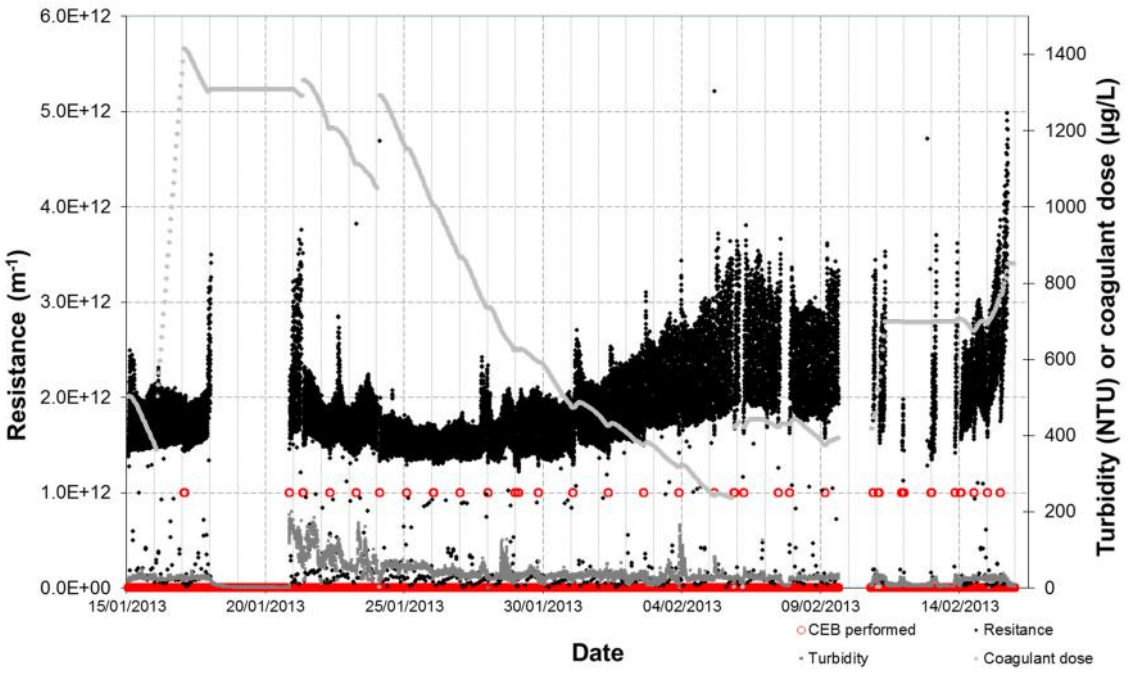

Figure 4.5. Hydraulic resistance (black symbols), feed water turbidity (dark grey symbols) and coagulant dose (pale grey symbols) evolution along time in winter conditions. Open circles, arbitrarily marked at $1E^{+12}$ m^{-1}, correspond to the moment when a CEB was performed.

As commented previously, the coagulant dose was automatically adjusted according to the system evolution. As can be seen in Figure 4.4 and Figure 4.5, the coagulant doses required in summer tended to be lower than in winter, which is in agreement with previous observations (Edzwald and Haarhoff, 2011, Pikkarainen et al., 2004). This finding can be due to different reasons, such as coagulant lower hydrolysis degree (Domínguez et al., 2005) and slower kinetics (Fitzpatrick et al., 2004) at colder temperatures, higher TOC content in water during winter (Edzwald and Haarhoff, 2011) and lower volume fraction of particles in feed water during winter (Tabatabai et al., 2009). pH, which is a key parameter in coagulation (Domínguez et al., 2005), did not present significant differences between winter and summer, as shown in Table 4.1. This hampered making any interpretation in terms of coagulation mode (charge-adsorption-neutralisation vs. sweep floc coagulation) in each scenario. However, according to Boulestreau and Miehe (2010), coagulation pH had a lower impact on the subsequent membrane permeability than the coagulant dose used.

In summer periods when Fe(III) dosage was above 1 mg/L approximately, hydraulic resistance increased faster than at lower doses and HC efficiency decreased in a notorious way (from 1.0 - 0.8 to 0.5 approximately, calculated by Eq. 4.1). Low resistance values could only be recovered by CEBs (Figure 4.4). In contrast, in winter time (Figure 4.5) the hydraulic resistance increased at a greater rate when doses were below 0.6 – 0.8 mg Fe(III)/L, presenting an opposite behaviour. In this case, HC efficiency was slightly decreased but to a much lower extent (from 0.9 to 0.8 approximately, calculated by Eq. 4.1). Judd and Hillis (2001) suggested that there was a coagulant dose threshold below which detrimental effects occurred: the flocs needed to grow above a certain critical floc size prior to challenging the subsequent membrane stage;

otherwise, an incomplete aggregation of colloidal particles and precipitated humic materials took place. On the other hand, Boulestreau and Miehe (2010) noted that an excessive coagulant dose had a negative effect on membrane filterability. Finally, Meyn and Leiknes (2010) stated that both over and under coagulant dose in comparison to its optimal requirements caused increased irreversible fouling. Wang et al. (2013) attributed these effects to an incomplete particle aggregation, due to the larger repulsion forces caused by the high charge imbalances. The small particles and low porosity for compressibility caused a tighter cake layer, deteriorating the permeability (Wang et al., 2013). The existence of an optimal coagulant dose to aid a subsequent membrane filtration could explain the discrepancies found in literature regarding impact of coagulation on filtration flux, because positive as well as negative effects have been reported (Barbot et al., 2008). Wiesner et al. (1989) concluded that those conditions which produced particles with a zeta potential close to zero, which also turned into aggregates size increase, minimised membrane fouling. Therefore, it can be hypothesised that on a first a stage the coagulant neutralises the particle surface charge, generating particles with sizes that form a cake of low hydraulic resistance. Afterwards, a further increase in coagulant dose reverses the particle charges, re-stabilising particles and forming cakes with high hydraulic resistance (Boulestreau and Miehe, 2010). Park et al. (2006) related cake resistance to size and fractal dimension of the aggregates. Fractal dimension provides insights into the aggregate structure, being low values (close to 1) attributed to open and highly branched assemblies and high values (close to 3) to compact and spherical structures (Barbot et al., 2008). Cakes formed by larger flocs present greater inter-floc permeability which turn into a significantly lower resistance than those created by smaller flocs (Lee et al., 2003). Veerapaneni and Wiesner (1996) determined, by numerical simulations, that fractal dimensions below 2 enabled the water to easily flow through the aggregates, with greater efficiencies at lower fractal dimensions. A good coagulation should form flocs with high porosity, be resistant to shear stress and have good intra-floc porosity (Boulestreau and Miehe, 2010).

The seasonal differences in the raw river water characteristics (e.g. foulants nature and content, physico-chemical properties, coagulant performance), might explain the dissimilarities in membrane performance observed in terms of coagulant need and over/under dosing effects (Figure 4.4, Figure 4.5). Futselaar et al. (2008) already remarked the need to continuously adapt the coagulant dose based on the seasonal and long term trends in water composition, modifications in operational conditions and progressive changes in membrane properties.

Figure 4.6 shows the hydraulic resistance evolution along each filtration cycle in every scenario considered. Because at the end of each filtration cycle a HC or a CEB took place, this graph represents the hydraulic resistance evolution from the end of a cleaning operation until the beginning of the next cleaning step. In order to assess the variability of the membrane behaviour, all filtration cycles performed during 1 month are depicted, leading to overlapping data. The purpose of the graph is to qualitatively evaluate the hydraulic membrane performance evolution during a filtration cycle, and to compare the hydraulic membrane behaviour between different filtration cycles.

In general, the higher the number of filtration run (between two consecutive CEBs), the larger the initial resistance after each HC (i.e. greater y axis). This suggested that the HC was not totally efficient, so that some fouling remained after an HC was conducted, but it could be partially removed by the subsequent CEB, lowering again the initial resistance. Because a relationship between CEB efficiency and accumulated operational time was not observed, membrane compactation effect might be minimal within these experiments, reinforcing the hypothesis that a non-completely efficient HC caused the increased initial resistance.

It can also be observed that despite the increased initial resistance in each filtration cycle, in general the resistance evolution was the same within each of the scenarios considered, not being dependent on the accumulated filtration time (Figure 4.6).

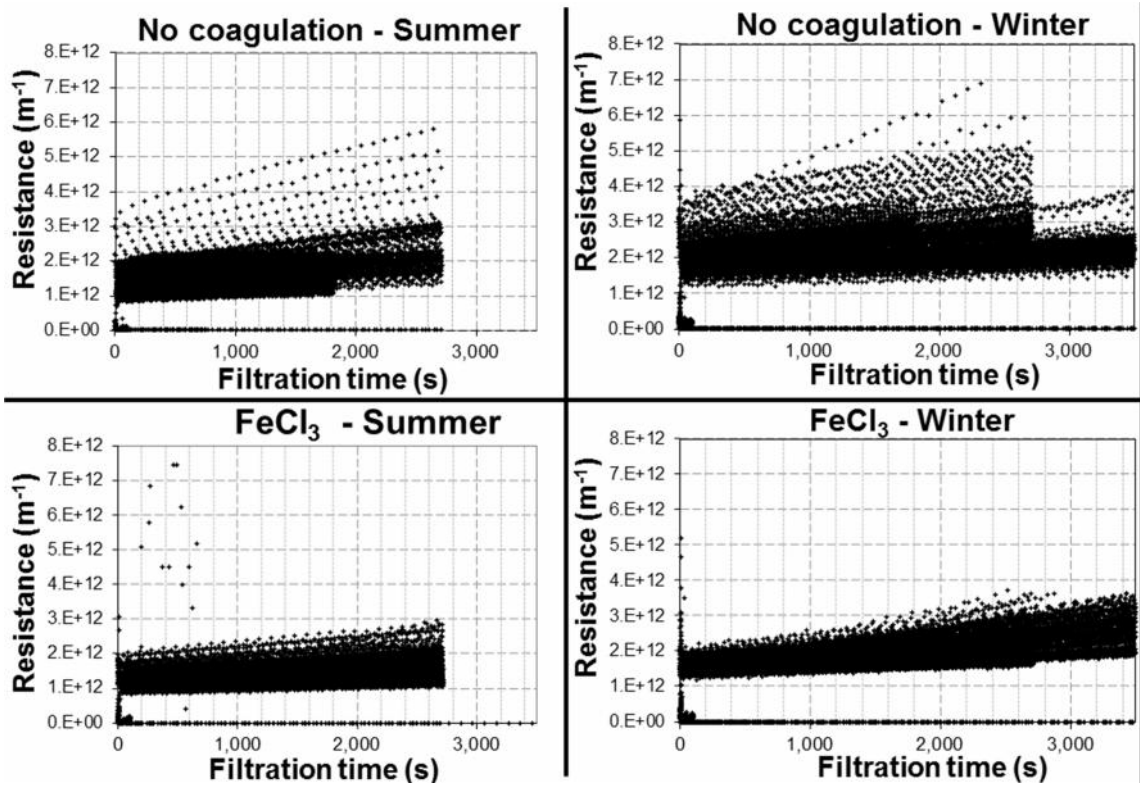

Figure 4.6. Hydraulic resistance evolution along time during each filtration cycle for one month under the following conditions: top left-hand side) summer no coagulation; top right-hand side) winter no coagulation; bottom left-hand side) summer coagulation; bottom right-hand side) winter coagulation.

When comparing summer/winter scenarios it can be seen that in winter there was a greater resistance increase along filtration time (Figure 4.6 right-hand side graphs vs. left-hand side ones), especially when no micro-coagulation was in place. This was in agreement with the lower flux attainable in a sustainable way during winter time when coagulant was not dosed.

The micro-coagulation reduced the rate of hydraulic resistance increase during each filtration cycle and also stabilised the process (Figure 4.6 top graphs vs. bottom ones). These effects were more pronounced in winter than in summer periods, which is also in accordance with the improvement experienced when micro-coagulation was put in place: in winter, attainable flux

increased from 40 L/(m^2·h) to 70 L/(m^2·h) (Table 4.2). The micro-coagulation had a positive effect on HC efficiency in both seasons, because the initial resistance in each filtration run (y axis) did not increase as much as when micro-coagulation was not in place.

In order to isolate the coagulant effect on cleaning efficiency and only focus on its effect during filtration, specific cake resistance was calculated by means of Eq. 4.3 (Table 4.3). As described later on, cake filtration was identified as the main fouling mechanism in all the scenarios addressed. The specific cake resistance was hence calculated, which indicated the increase of the foulants cake layer resistance build up in each case. As depicted, hydraulic resistance increase rate was higher in winter than in summer, which is in agreement with the hydraulic conditions attainable previously described. It was particularly high in the no coagulation – winter scenario. In this case, the average specific cake resistance was around 6 fold greater than coagulation – winter condition and presented a much larger deviation (180 fold approximately). Therefore, the dosage of ferric chloride significantly stabilised the filtration process in winter. This was in agreement with the more demanding conditions in terms of filtration flux the membrane could handle. In summer, the average specific cake resistance was lowered 2.5 fold approximately and its associated standard deviation 10 times when the micro-coagulation was conducted. The coagulant impact on filtration was more remarkable during winter time, but in all conditions led to positive effects, decreasing the rate of hydraulic resistance increase during filtration and stabilising the process.

Table 4.3. Specific cake resistance statistics under the four conditions considered (coagulation / no coagulation, summer / winter).

α (m^{-2})	Minimum	Maximum	Average	St. deviation
No coag - Summer	$5.0E^{+12}$	$1.8E^{+15}$	$1.8E^{+13}$	$5.0E^{+13}$
No coag - Winter	$5.7E^{+11}$	$2.4E^{+16}$	$7.5E^{+13}$	$1.1E^{+15}$
$FeCl_3$ - Summer	$3.6E^{12}$	$1.0E^{+14}$	$7.5E^{+12}$	$4.8E^{+12}$
$FeCl_3$ - Winter	$5.7E^{+12}$	$4.5E^{+12}$	$1.3E^{+13}$	$6.0E^{+12}$

Literature has reported cake filtration as main fouling mechanism when in-line coagulation has been applied, eliminating pore blockage (Huang et al., 2009, Tabatabai et al., 2009). In order to determine whereas a different fouling mechanism prevailed in winter/summer, coagulation/no-coagulation, the experimental data obtained was fitted to the traditional blocking laws models (complete blocking, standard blocking, intermediate pore blocking and cake filtration) for constant flow filtration (Hlavacek and Bouchet, 1993, Iritani, 2013). Transmembrane pressure $(TMP)^{-1}$ vs. filtered volume (V), $(TMP)^{-0.5}$ vs. V, ln(TMP) vs. (V) and TMP vs. V, were plotted representing the abovementioned blocking laws respectively, for each scenario. In all the cases, cake filtration seemed to be the mechanism which better described the experimental data according to the regression coefficients (R^2) obtained. However, it is important mentioning that regression coefficients obtained per blocking mechanism did not differ between them to a large extent. This could partially be due to the working pressure range, between 0.09 and 0.53 bar for the considered periods, which made most of the models fit quite well (R^2: 0.91 – 0.98). Experiments performed under constant filtration flow successfully identifying the main fouling mechanism by fitting the different models to the experimental data obtained reported in literature (Chellam and Xu, 2006, Hlavacek and

Bouchet, 1993, Iritani et al., 2015) used a wider pressure range. They were conducted at bench scale, and thus, hydraulic conditions could be forced. In this study, the hydraulic operational conditions required by the full scale system were limited (TMP < 1 bar, hydraulic resistance < $1E^{+13}$ m^{-1}). If wider pressure ranges could have been implemented more significant differences might have been encountered. Additionally, the discrepancies between the process conditions and the model assumptions, as well as the existence of several mechanisms occurring simultaneously, might difficult a better fitting.

Assuming the set up limitations and based on the regression coefficients obtained, cake filtration could be suggested as the prevailing blocking mechanism in all the scenarios. Then, blocking laws would not explain the membrane hydraulic differences experienced in summer / winter, coagulation / non-coagulation. Consequently, it might be the fouling cake characteristics which caused the different membrane filtration behaviour experienced. This would be in accordance with Jermann et al. (2008), who stated that the flux decline was determined by the morphology of the fouling cake, whereas the fouling reversibility by the interaction between the cake layer and the membrane surface.

Previous works observed that cake porosity was much higher when coagulation was in place (93% vs. 37%) (Doyen et al., 2003), which could explain the performance observed. More porous cakes have been related to lower TMP increases (Doyen et al., 2003) since they present diminished resistance (Sripui et al., 2011). Similarly, less compressible cakes have been claimed to cause the same effect (Salinas Rodríguez, 2011): Heijman et al. (2005) reported a 2 fold decrease in compressibility approximately due to coagulation. Nevertheless, because of working continuously with highly variable surface water at pilot level, it was not possible to determine such characteristics of the foulants cakes formed and relate them to the observed effects of micro-coagulation on membrane performance.

ii) Coagulant effect on hydraulic resistance recovery by HC and CEB

HC cleaning efficiency in the four scenarios envisaged was calculated by means of Eq. 4.1 and its associated statistics are shown in Table 4.4.

Table 4.4. HC efficiency statistics under the four conditions considered (coagulation / no coagulation, summer / winter).

HC efficiency	Minimum	Maximum	Average	St. deviation
No coag - Summer	0.45	1.14	0.74	0.13
No coag - Winter	0.57	1.14	0.87	0.09
$FeCl_3$ - Summer	0.45	1.12	0.86	0.11
$FeCl_3$ - Winter	0.57	1.50	0.92	0.07

As can be seen in Table 4.4, in average terms, the HC was more effective in winter than in summer regardless of coagulant dosage (significance 0.05). Taking into account that the HC sequence and conditions were not modified during the whole study, it can be concluded that in winter, either less foulants were accumulated between HCs turning into a more efficient HC, or that foulants were more easily removed by the HCs. In this regard, BPs, by virtue of its high MW and size, are mostly retained by cake formation, and thus, amenable to be washed out by

HCs (Gibert et al., 2015). BPs concentration in raw river water was higher in winter, which would be in accordance with the greater HC efficiency experienced. On the other hand, raw water physico-chemical characteristics (Table 4.1) showed a greater turbidity and TSS content in summer which would support the hypothesis of higher foulants load accumulated in summer periods.

The micro-coagulation resulted in a significant increase in HC efficiency, both in summer and in winter (5 and 15% respectively; 0.05 significance), which is in accordance with Zupančič et al. (2014), as well as a decrease in its variability. Different effects of cakes have been reported: "inert cakes", which act like a pre-filter screening those materials with a high fouling potential avoiding their direct interaction with the membrane, and "adhesive cakes", which are formed by foulants glued to the membrane surface and entrap inert deposits (Shi et al., 2014). In this study, probably the coagulant dosage enabled the formation of a cake which acted like a filter aid, preventing molecules with a high fouling potential reaching the membrane. This probably led to a cake more easily removed by physical means.

Table 4.5 presents the CEB efficiency for the four scenarios considered, calculated by Eq. 4.2 means. Unlike the HC efficiency, the average CEB efficiency in winter was significantly below the one in summer. This was expectable, because in order to increase chemical cleanings efficiency heating is an option commonly adopted, and in summer water temperature was higher than in winter (26.5 vs. 8.9 ºC on average). This could be attributed to augmented kinetics of the reaction between foulants and cleaning agents, their increased solubility and/or the greater diffusion and reaction rates at higher temperatures. Also, the chemical nature of the fouling itself according to the season might have an impact, being more physically irreversible in summer, and thus, leading to a lower HC efficiency in those conditions, but presenting greater CEB efficiency. When comparing coagulation / non-coagulation, it could be seen that in winter there was an increase in efficiency (0.36 vs. 0.42) and a slight stabilisation of the variability (0.05 vs. 0.040), whereas in summer there was a decrease in efficiency (0.61 vs. 0.57) and in variability (0.07 vs. 0.10). In this case the coagulant performance may also contribute to the different trends observed.

Table 4.5. CEB efficiency statistics under the four conditions considered (coagulation / no coagulation, summer / winter).

CEB efficiency	Minimum	Maximum	Average	St. deviation
No coag - Summer	0.48	0.73	0.61	0.07
No coag - Winter	0.26	0.48	0.36	0.05
$FeCl_3$ - Summer	0.36	0.73	0.57	0.10
$FeCl_3$ - Winter	0.34	0.49	0.42	0.04

4.4. Conclusions

Direct UF of raw river water proved to be a technically feasible and competitive alternative to conventional DWTP pre-treatment process (dioxichlorination, coagulation, flocculation / settling and sand filtration), enabling a continuous operation regardless of incoming water quality fluctuations (e.g. turbidity 5 - >1000 NTU) and to deliver a product water of equal or superior quality to the current one for most of the parameters monitored. Despite the challenging position of the UF membrane (raw river water direct filtration) no integrity problems were encountered during the two years evaluated.

Hydraulic membrane performance differed between seasons, achieving higher filtration fluxes in summer. This could be due to the membrane properties as well as the feed physico-chemical water characteristics, especially in terms of foulants nature and content. DOC concentration was higher in winter periods, with greater BPs content, which have been claimed to be main membrane foulants.

Based on the greater HC efficiency experienced, foulants in winter tended to form a looser cake or lower amounts were accumulated. However, the cake presented higher resistance, leading to larger hydraulic resistance increase during filtration. It can be hypothesized that in summer a more porous cake was formed, which caused a lower pressure drop, but it was more tightly bound to the membrane, provoking a lower HC efficiency. Alternatively, larger amounts of foulants were accumulated into/onto the membrane which could also provoke a diminished HC efficiency.

Performing a ferric chloride micro-coagulation upstream the UF membrane in winter enabled a significant increase in bearable conditions. As a result, the seasonal variations in attainable filtration fluxes were decreased, enabling the implementation of similar conditions in summer and in winter. This would be preferred from an engineering standpoint, since a system with overcapacity in summer periods would be avoided, as well as lower investment in terms of membrane modules would be needed. The micro-coagulation also reduced by half the chemically based cleaning operations frequency in all the conditions addressed.

In winter, the benefits of micro-coagulation were mainly in the filtration stage, since specific cake resistance was lowered around 6 fold and was significantly stabilised (standard deviation decreased 180 times approximately) when it was applied. This could be due to the formation of a more porous cake, leading to a lower hydraulic resistance gain over each filtration cycle. HC and CEB cleaning efficiencies were also improved, but to a lesser extent. In summer periods, the micro-coagulation also affected positively the filtration stage, reducing by a factor of 2.5 approximately the specific cake resistance and stabilising it, and slightly increasing the HC and decreasing the CEB efficiencies. Larger coagulant doses were needed to build up cakes with the desired characteristics (high permeability and strength according to Pikkarainen et al. (2004) in winter compared to summer, being under-dosing more detrimental in winter and overdosing in summer.

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CHAPTER 5

Definition of ultrafiltration integrity tests based on virus surrogates

This chapter is based on:

Ferrer, O., Casas, R., Galvañ, C., Lucena, F., Vega, A., Gibert, O., Jofre, J., Bernat, X., 2013, Challenge tests with virus surrogates': an accurate membrane integrity evaluation system?. Desalin. Water Treat., 51, 4947-4957

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Abstract

The use of membrane filtration in drinking water treatment has significantly increased in the last decades due its advantages, including its capacity to produce water of high quality with a high level of pathogens rejection. However, if membrane integrity is compromised, this feature cannot be guaranteed, increasing the associated microbial risk of the treated water. This chapter focused on the development and application of a protocol based on viruses surrogates challenge tests applicable to the three existing ultrafiltration configurations: pressurised inside-out, pressurised outside-in and submerged outside-in. The operational conditions under which it should be run were defined and the tests were conducted successfully. The selected microorganisms, PDR-1, MS-2, GA and *Bacillus* spores, present different characteristics providing complementary information of membrane integrity and its status. In particular, PDR-1 and *Bacillus* spores, due to their larger size, are mainly removed by size exclusion and low removal rates might indicate membrane impairment. MS-2 and GA, 25 nm in size approximately, might not be rejected by size exclusion but by adsorption and electrostatic interactions, so that their removal values might not necessarily be indicative of membrane integrity failures. Since they might be influenced by further factors, such as membrane characteristics, feed water quality, non-chemically removable fouling, etc., the results obtained can be used to better understand membranes performance.

5.1. Background

During the last decades membrane technology has significantly evolved, becoming a technological solution increasingly applied in drinking water treatment plants (DWTPs) due to its advantages. Among them, it is remarkable its capacity to produce high quality treated water independently of incoming water quality fluctuations. High levels of pathogens rejection can be achieved, as demonstrated by several researchers who proved a complete removal of coliform bacteria, *Giardia spp*. and *Cryptosporidium spp.* by low pressure membranes, which include microfiltration (MF) and ultrafiltration (UF) (Guo et al., 2010). Due to the lower cut-off of UF membranes compared to MF ones, the former present some disinfection capacity, being able to remove a percentage of viruses as can be seen in Figure 5.1. The high product water quality obtained by membrane processes, linked to their reliability, modularity (and thus, easiness to scale-up), reduced space requirements, operation easiness, possibility of being automatised and relatively low cost has led to their recognition as promising processes for water treatment. Consequently, the global installed volume of low pressure membrane systems has increased almost exponentially (Gimbel, 2003), being 60% of its applications for drinking water treatment (David et al., 2008).

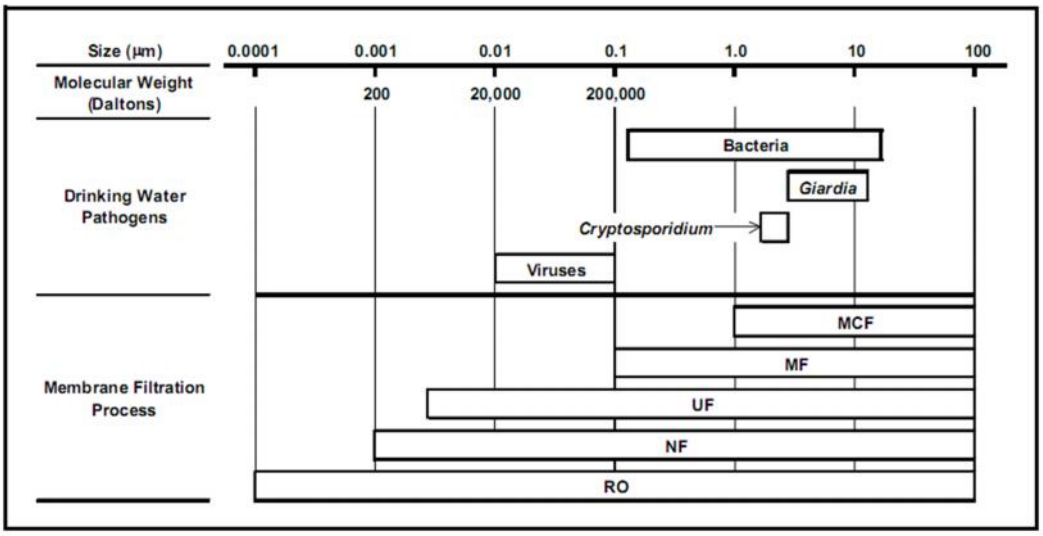

Figure 5.1. Approximate retention spectrum of different water borne pathogens and membrane filtration processes capacity to remove them, based only on size exclusion. NF: nanofiltration, RO: reverse osmosis, MCF: membrane cartridge filtration (US EPA, 2003).

Although MF or UF membranes represent a theoretical absolute physical barrier to particles (pathogens, indicators, suspended solids, etc.) that are larger than the membrane pore size, they can suffer damages that lead to a decline in permeate quality. Therefore, if membrane integrity is compromised, pathogen may pass through it and thus, contaminate the product water. Failure of membrane fibres may be due to several reasons: i) chemical corrosion (e.g. oxidation); ii) defective installation and maintenance; iii) operational conditions causing membrane stress and strain (e.g. backwash, vigorous bubbling); iv) impairment by sharp objects not removed in the pre-treatment (Guo et al., 2010). Zondervan et al. (2007) identified several aspects that may act as significant ageing agents and hence, contribute to membrane

failure: membranes fouling degree, the number of applied back pulses and the combination of these two factors.

Membrane integrity is a critical aspect for any membrane filtration plant in order to minimise its associated microbial risk. The minimisation of microbial risk involves demonstrating that the membrane system can adequately remove pathogens and the periodic and/or continued verification that the membrane is intact. The United States Environmental Protection Agency (US EPA) established through different pieces of legislation (Surface Water Treatment Rule (SWTR) 1986; Interim Enhanced Surface Water Treatment Rule (IESWTR), 1998; Long Term 1 Enhanced Surface Water Treatment Rule (LT1ESWTR), 2002; Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR), 2006) target removal values for the whole water treatment process as well as for the membrane based filtration process for certain pathogens. Additionally, this organisation defined the testing procedures to be implemented to validate the $\log_{10}$ removals of membrane filtration processes (challenge tests, conducted in the framework of the Environmental Technology Verification (ETV) programme) and the surveillance tests (direct integrity testing and continuous indirect monitoring) to be conducted to ensure the log removals previously obtained in the challenge tests. Integrity testing represents a practical way of verifying the barrier effectiveness by detecting leaks or membrane breaches and can be measured by direct and indirect methods (Guo et al., 2010), such as the quantification of certain pathogens (or their surrogates) removal rates. However, membrane integrity tests have to be adapted to each specific membrane and, in the case of surrogates challenge tests, testing conditions are not sufficiently defined in the US EPA membrane filtration guidance manual (2003).

Due to these limitations, this work focused on the development and application of a membrane integrity testing protocol applicable to the three basic configurations of UF hollow fibre technology: pressurised inside-out, pressurised outside-in and submerged outside-in. For such purpose, different surrogates were selected and appropriate testing conditions were defined, aiming at determining the most convenient model organism and the testing operational settings. The results obtained were compared with conventional pressure decay tests (PDTs) in order to assess the reliability and accuracy of the approach adopted. The limitation of the PDT tests has been reported in literature, concluding that plants relying solely on this method may work beyond the point where the integrity is compromised because it cannot guarantee viruses removal (Guo et al., 2010). The pressure used in the PDTs determines the minimum defect size to be identified. For a defect size of 3 µm, as stipulated in the LT2ESWTR to be achieved by membrane processes, the pressure needed, adopting a conservative approach, would be 1 bar, for 1 µm defect 3 bar, for 0.1 µm defect 30 bar and for 0.02 µm defect (virus size) 150 bar. Therefore, to identify defects below 1 µm, the pressures required are excessive and unviable to be implemented in UF systems.

Membrane integrity monitoring based on permeate characteristics such as turbidity or particle counting enables a continuous follow up of the membrane systems. Nevertheless, the identification of permeate quality decrease typically requires a significant impairment of the membrane, so that more precise tools are needed to complement these routine testing.

5.2. Materials and methods

5.2.1. Surrogates selection and quantification

Three different bacteriophages were selected to undertake this work: MS-2, GA and PDR-1, as well as *Bacillus* spores as a control due to its larger size. The latter can be considered as a surrogate of *Cryposporidium* (Chauret et al., 2001, Nieminski, 2002, Nieminski et al., 2000, Radziminski et al., 2002). Bacteriophages were selected because they are similar to enteric viruses (phages share many properties with human viruses in terms of composition, structure, morphology and capsid size), they are innocuous to humans and high titers can be obtained in the laboratory. MS-2 and GA have the same size (25 nm approximately) but differ in isoelectric point and hydrophobicity, presenting a different tendency to adsorb onto solids and to aggregate (Langlet et al*.,* 2008). In particular, they are considered the extreme cases in terms of membranes adsorbability, so that the behaviour of the great majority of human viruses in this respect will be in between MS-2 and GA. PDR-1 is 60-70 nm in size, and *Bacillus* spores about of 900 to 1600 nm. The surrogates retention mechanisms are size exclusion (for those surrogates whose size is greater than the membranes pore sizes), adsorption and electrostatic forces.

Quantification of *Bacillus* spores in 10 mL aliquots of the samples were enumerated by pour plate technique using an adapted *Bacillus* specific medium after a thermal shock at 80ºC during 10 minutes. Plates were incubated at 30 ºC during 48 to 72±3 h. The limit of detection of the technique was 10 colony forming units (CFUs) per L. Regarding bacteriophages quantification pre-filtered samples were quantified without bacteriophages concentration. In the case of UF permeate samples, bacteriophages were concentrated. Bacteriophages were enumerated by the double agar layer method described by Adams (1959). GA and MS-2, which are F-specific RNA bacteriophages, were enumerated according to ISO standard 10705-1 (International Organization for Standardization (IOS), 1995); and PDR-1, which is a somatic coliphage, according to ISO 10705-2 (IOS, 2000), but using host strain *E. coli* MS1000 instead of *E. coli* WG5 used for somatic coliphages. The limit of detection of the technique was 1 plaque forming unit (PFU) per L in pre-filtered samples and 0.001 PFUs per L in the UF permeates.

The logarithmic removal values (LRV) obtained, calculated by Eq. 5.1, provided information about the integrity of the membrane fibres. C_f and C_p represent the concentration of the surrogate under consideration in the feed and permeate stream respectively. C_f is also referred as the spiked concentration and denotes the surrogates concentration that the membrane faces in each challenge test.

$$LRV = \log\left(\frac{Cf}{Cp}\right) \qquad \text{Eq. 5.1}$$

The LRV awarded to each membrane in each challenge test was calculated as the arithmetic mean of the three LRV obtained at the three different sampling times of each experiment.

LRV for *Bacillus* spores were calculated theoretically, apart from experimentally measured, based on LT2ESWTR (Eq. 5.2), which relates the pressure drop recorded during the PDT with

the removal rates. Q_p stands for the permeate flow, Q_{breach} the flow passing through an impaired fibre and VCF the volumetric concentration factor.

$$LRVt = \left(\frac{Qp}{VCF \cdot Qbreach}\right) \qquad \text{Eq. 5.2}$$

Full scale membrane modules with different pore sizes (ranging from 20 to 40 nm) and characteristics (membrane material, configuration, etc.) were used to assess the suitability of the method developed. The tests were conducted every three months approximately to the same membrane modules, which were in continuous operation for direct surface water pre-treatment demonstration, to assess their integrity and changes suffered over time. When data is not shown in the graphs it was due to an operational or analytical problem so that results were not obtained.

5.2.2. Challenge test protocol definition

The test consisted in undertaking a chemically enhanced backwash (CEB) to the membrane, adjusting the feed water (dechlorinated tap water) conductivity, inoculating a known stock concentration of bacteriophages/spores and evaluating the concentration over time both in the feed and permeate streams during filtration. It was important to conduct the test without coagulant dosage (some coagulants entrap and adsorb in/on flocs and present virucidal activity, such as the aluminium based ones (Matsui et al*.,* 2003, Shirasaki et al., 2009a, 2009b)) nor pH correction because of its effect on adsorption (Matsui et al., 2003, Shirasaki et al., 2009a).

The CEB was performed following the recommendations of the membrane manufacturer in terms of chemicals used, concentration, stages applied and duration. The aim of the preliminary chemical cleaning was to remove the membrane deposits and hence, leave the membrane defects, if existing, uncovered. Feed tank was cleaned and tap water was introduced and dechlorinated by adding sodium tiosulphate (0.1 mol/L; J.T. Baker). Sodium chloride (99.0% purity; J.T. Baker) was then added to the feed water tank to adjust its conductivity to 2,000 µS/cm. As a result, the ionic strength of the testing solution was kept constant between experiments and it could be achieved in each challenge test trial.

After 10-30 min of feed tank stirring (this value depended on the characteristics of the testing facility used), the system was forced to filter for 2 minutes (this value was based on the characteristics of the testing facility used as well) in order to flush the piping and determine the initial membrane resistance, which enabled the establishment of the fouling level of the membrane. Bacteriophages and/or spores were then spiked in the feed tank. Due to the characteristics of the detection methods of the surrogates used, MS-2 was spiked together with PDR-1 and GA with *Bacillus* spores*.* The protocol had thus to be applied twice. The seeding concentration of the surrogates was selected in such a way to prevent surrogates aggregation, which would overestimate the system removal capacity, as recommended by the LT2ESWTR (2006).

Feed tank agitation for 20-45 min (this value depended on the characteristics of the testing facility used) was applied to ensure homogeneous solution of the surrogates in the feed tank. Subsequently, the system started filtration at a given constant flow (30 - 40 L/(m^2·h) depending on the membrane), without applying any backwash (BW) nor CEB cycle. The filtration flux was selected below the maximum nominal value of each tested membrane, because these tests were planned to be carried out during the membrane lifetime. Therefore, in case of suffering severe non-chemically removable fouling, it might be difficult to achieve or sustain a high flow during the challenge test, especially because no BWs and CEBs should be conducted. The US EPA, to quantify a membrane removal credit, suggests testing the membrane at its maximum nominal flow. This test is only done once in the membrane lifetime, so more sever conditions can be applied. ETV trials showed that the MS-2 LRVs were inversely proportional to the flux applied. However, within the same study, it was also observed that the LRVs for the lower flow rates were all within the range of the LRVs from the maximum flux test. Consequently, in the protocol developed in this work, the selection of flow rates below the maximum nominal values was considered appropriate.

Feed and permeate samples were taken simultaneously at a given time, three times along the test (e.g. 5, 10, 15 min, according to the autonomy of the testing system). Several process parameters were monitored during the test, such as turbidity, conductivity, pH, temperature and transmembrane pressure (TMP). After the test, the system was drained, cleaned and filled with the water source normally treated (raw surface water), and a CEB was performed to ensure the removal of the surrogates from the system.

Since the water used for the tests was tap water, no significant fouling was being deposited during the test performance, and hence, the effect of adsorption to physically removable fouling or cake layer formation was minimised. Therefore, surrogates removal was ensured to be due to size exclusion, membrane adsorption and non-chemically removable fouling, but not due to particulate material either in suspension or deposited onto the membrane. According to Lozier et al. (2003), integrity defects on the order of 200 µm can be masked by foulants, improving pathogen rejection. To determine whereas fouling occurred during the test and if so, its impact in the surrogates removal rate, the LRVs and the membranes resistance along time were plotted and no differences were encountered (data not shown). This was in accordance with Martí et al. (2011), who undertook challenge tests with virus surrogates in membrane bioreactors.

Pressure Decay Tests (PDT) tests were conducted just after the initial CEB performed, when potential membrane defects were uncovered, to compare both results. During the PDT, the membrane module was drained, compressed air (below the bubble point and above the pressure needed to determine a given defect) was supplied to the drained side of the wetted membrane and the pressure was maintained for a given time. In case of membrane integrity failure, the airflow through the pores would be orders of magnitude higher than the diffusion flow that would occur if the membrane integrity was not damaged. By measuring the pressure drop, the membrane integrity could thus be determined.

5.3. Results and discussion

5.3.1. Bacillus spores tests

Figure 5.2 shows the LRV obtained for the four challenge tests conducted in the three membrane modules (bars) as well as the spiked concentration (C_f, dots) in each case. As can be seen, the LRVs average ranged from >3.9 to 5.2, indicating high removal. The SWTR (from 1986) requires 3 $\log_{10}$ removal of *Giardia*, which is slightly larger in size than *Cryptosporidium*, for the whole water treatment. Taking into account that the latter is more difficult to eliminate than *Giardia* (Health Canada, 2010*)*, based on the results obtained, the membrane treatment itself was capable of removing at least approximately 1 more $\log_{10}$ than the established threshold for *Giardia*. As a result, the membranes alone would enable the fulfilment of this rule. The LT2ESWTR (from 2006), based on the incoming water quality, requires different removal credits for *Cryposporidium*, ranging from 0 to 5.5 LRV for the whole treatment process. Considering the values obtained, the tested membranes would only require 1.5 more $\log_{10}$ removal to fulfil the most stringent requirement for the whole process, which would typically be achieved with coagulation-flocculation-sedimentation (World Health Organisation, (WHO), 2004), or coagulation itself (Lee et al., 2007) or to a larger extent by UV disinfection (US EPA, 2006).

In the case of membrane A, differences found in the various tests conducted (Figure 5.2 black bars) were not significant since their average LRVs values were 4.5, >4.4, >4.9, 4.8, so they differed in less than 0.5 $\log_{10}$ units. However, it is important to remark that, in the second and third challenge test, the permeate concentration was below the detection limit. Therefore, greater removal rates might have been obtained. Membrane B also performed nearly constant along the various tests, presenting average LRVs values of 4.4, 4.8, >4.3, 4.9, which also varied in 0.5 $\log_{10}$ units (Figure 5.2 grey bars). In the penultimate test, *Bacillus* spores permeate concentration was below the detection limit. Thus, a greater removal rate might have been achieved. Membrane C increased the LRVs obtained, being their average values >3.9, >4.4 and 4.6 (Figure 5.2 white bars). Nonetheless, *Bacillus* spores concentrations in the permeate were below the detection limit in the first two tests. As a result, the seeding stock concentration was increased accordingly (3.0, 3.4 and 3.8 $\log_{10}$) in order to enable a precise quantification. This explained the increase in LRVs between tests concerning the membrane C.

It is important to highlight that, due to the fact that the test objective was to evaluate the suitability of the developed integrity protocol in the three UF configurations, the different membranes results should not be compared directly since their characteristics as well as the operational conditions applied were different.

Theoretical LRV (LRV_t) for *Bacillus* spores based on the LT2ESWTR equation (Eq. 5.2) differed from the real values obtained between 0.5 – 1.0 $\log_{10}$ units (15 – 20% in absolute terms). This difference could be attributed to the conservative approach taken when calculating it from a theoretical point of view, leading to lower removal values than the real ones. Nonetheless, the

error obtained appeared as acceptable especially if conducted as a routine test complemented by other more accurate procedures which enable the detection of defects below 1-3µm.

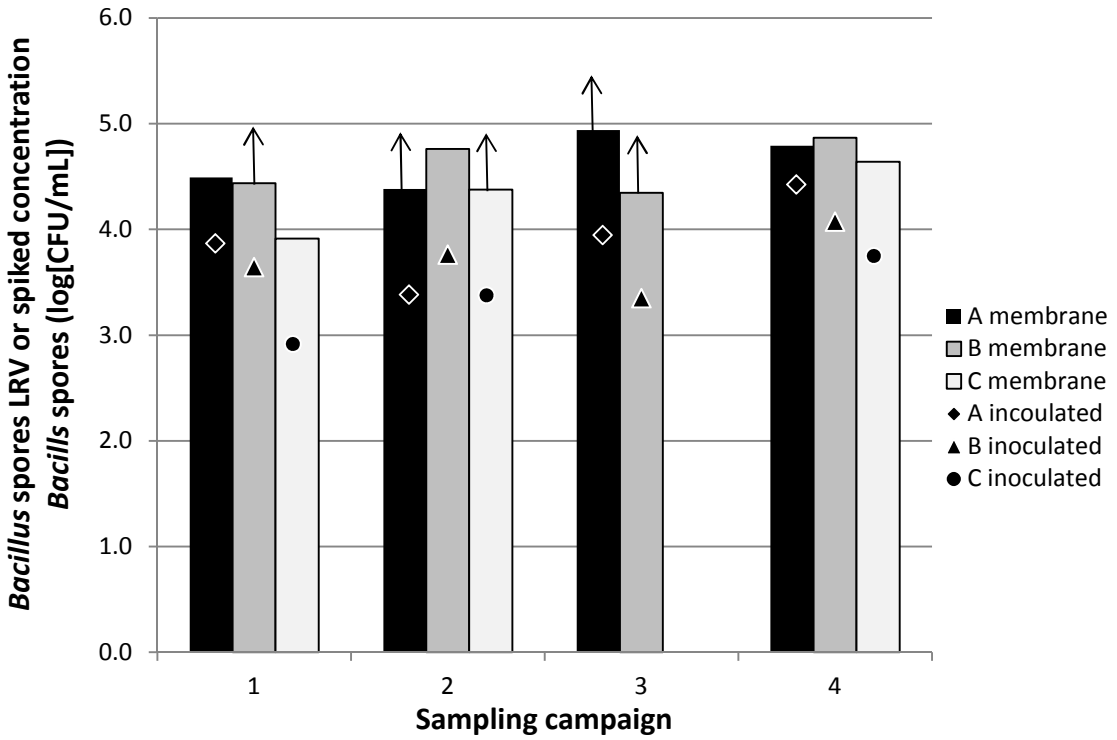

Figure 5.2. LRVs (bars) and spiked concentration (dots) of *Bacillus* spores of the three membrane modules tested in the four challenge test trials performed. Black bars correspond to A membrane, grey ones to B membrane and white ones to C membrane. Diamond, triangle and circle symbols correspond to the spiked concentration in each test to A, B and C membranes respectively.

5.3.2. Bacteriophages tests

The characteristics of the bacteriophages used enabled the testing of membrane integrity as well as their capacity to remove enteric virus surrogates. Because of the size of **PDR-1**, around 60 nm, it should be removed by all the membrane systems tested due to size exclusion phenomena. The presence of this phage in the permeate streams would indicate that the membrane fibres were compromised. Figure 5.3 shows the LRVs of the different membranes tested (bars), which ranged between 3.6 and 7.1 $\log_{10}$, as well as the PDR-1 spiked concentration (dots).

For all membranes, in all the campaigns except the second for membrane A and the first for membrane C, the PDR-1 concentration in the permeate was below the detection limit. However, the seeded concentration in the third test was an order of magnitude lower than in the previous cases, which explained the lower LRVs values obtained. In the fourth campaign the detection limit was decreased in 2 $\log_{10}$ units due to analytical issues, and similarly did the LRV obtained.

Despite the apparent decrease in the PDR-1 LRVs experienced, it was remarkable the fact that LRVs were quite high, suggesting that the membranes were intact during the tested period (1 year approximately). As pointed out previously, the direct comparison between membranes might not be adequate due to the differences in the seeding concentration (even though they were supposed to be minimised), the operational conditions tested during their lifetime, etc.

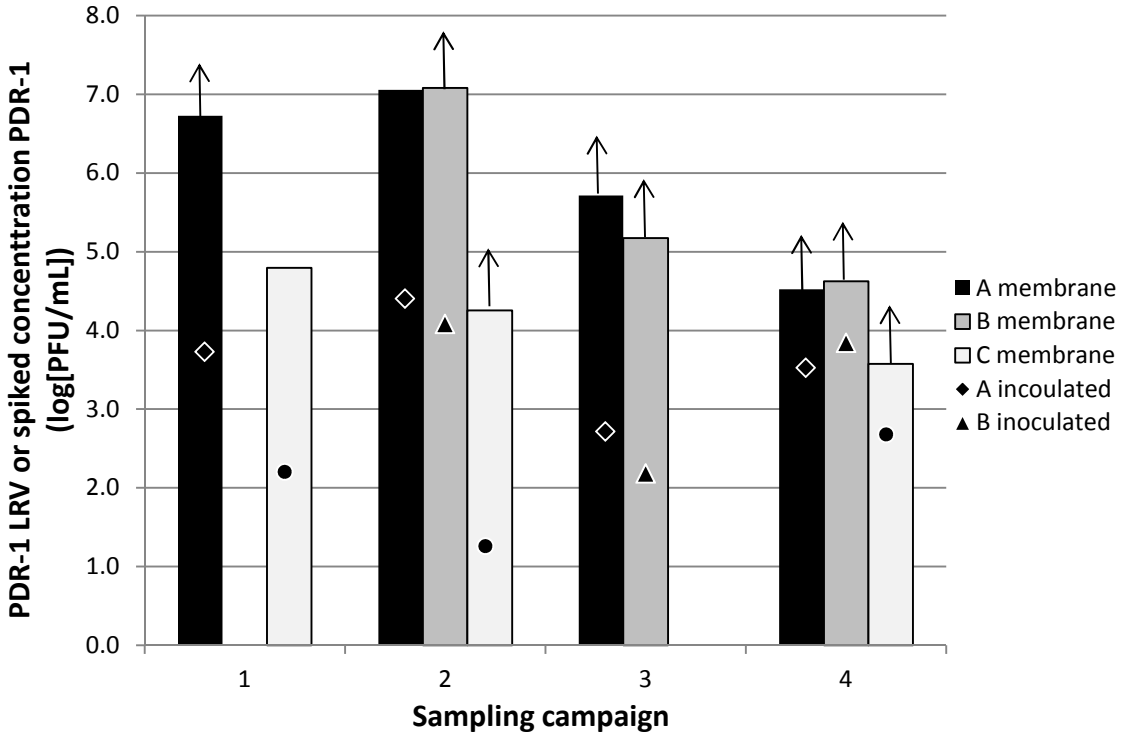

Figure 5.3. LRVs (bars) and spiked concentration (dots) of PDR-1 of the three membrane modules tested in the four challenge test trials performed. Black bars correspond to A membrane, grey ones to B membrane and white ones to C membrane. Diamond, triangle and circle symbols correspond to the spiked concentration in each test to A, B and C membranes respectively.

MS-2 and **GA** present smaller dimensions than the previous surrogates and are in the range of, or even slightly minor than, the membrane pore sizes tested (20-40 nm). Consequently, their removal rates were expected to be lower, and they should not be taken as straightforward indicators of membrane integrity but as an evocation of changes in the membrane properties, which could preclude future damages.

Figure 5.4 and Figure 5.5 represent the LRVs per MS-2 and GA respectively for the three tested membranes as well as their spiked concentration. Due to operational issues, membrane C could not be tested in the second and third campaign. MS-2 was used in previous works to assess membrane integrity (Jancangelo et al., 1997, Kruithof et al., 1998, Langlet et al., 2009, Oh et al., 2007, Zhu et al., 2005, Zodrow et al., 2009) and it was considered as a "worst case scenario" in terms of virus removal (Boudaud et al., 2012).

As can be seen, in this case the average LRVs fluctuated to a larger extent than with the previous surrogates: in the case of membrane A 2.1, 1.4, 2.4 and 1.8 LRVs (Figure 5.4, black bars); for membrane B 3.2, 2.2, 1.3 and 2.8 LRVs (Figure 5.4, grey bars) and for membrane C 5.6, 2.7 LRVs (Figure 5.4, white bars). This might be explained by the main separation mechanism. With these smaller surrogates, adsorption and electrostatic interactions play a more significant role. As a result, the membrane fouling deposited (non-chemically removable) might lead to a greater surrogates retention. Consequently, the membrane resistance after the initial CEB divided by the virgin membrane resistance was taken into account in all the experiments to identify potential differences originated from remaining fouling. Martí et al. (2011) reported that viral indicators LRV depended on irreversible fouling (not removable either by physical and chemical means), expressed by TMP, accumulated in the membrane. Nonetheless, the results obtained from September 2011 until July 2012 did not show a clear relationship between the resistance when starting the experiment and the virgin membrane resistance with the LRV obtained. However, since the experiments took place at different seasons (i.e. distinct water quality), fouling composition deposited on the membrane might be different and thus, present a dissimilar behaviour, enhancing or not removal rates. Besides fouling nature, the membrane properties themselves (hydrophobicity and electrical charge mainly), both virgin and after continuous operation, might also be responsible for this variability.

Regarding membrane C, the large LRVs differences encountered could be attributed to a larger particle content in the water used for the first trial (a turbidity increase was experienced in the water where viruses were spiked). This might have enhanced the association of bacteriophages (Templeton et al., 2007), becoming more easily retainable by the membrane and hence, overestimating their removal rates.

Even though LRVs obtained were significantly lower than the 4 $\log_{10}$ recommended by the USEPA for the whole treatment (SWTR (US EPA, 1986)), it is important to take into account that the size of these bacteriophages is normally smaller than UF membranes pore size, so their removal only by size exclusion is not feasible. DWTPs based on membranes would encompass at least a final disinfection step, which is able to inactivate viruses in an easier way than other organisms like oocysts, which are highly resistant to chlorine and chloramines (US EPA, 2003). In this sense, the *Bacillus* spores testing previously described would ensure the system removal capacity of this protozoan parasite and the final disinfection stage the viruses.

Figure 5.5 represents the LRV (bars) of each challenge test concerning GA and their spiked concentration (dots). Membrane A average LRVs were 1.2, 1.1, 1.3 (black bars), B membrane 2.0, 1.8, 1.4, 2.0 LRVs (grey bars) and 3.2, 2.9, 2.7 LRVs for C membrane (white bars). Analogously to MS-2 due to the separation mechanism nature, further factors such as deposited fouling and membrane characteristics might explain the fluctuation. Nevertheless, the variability was smaller than in the previous case.

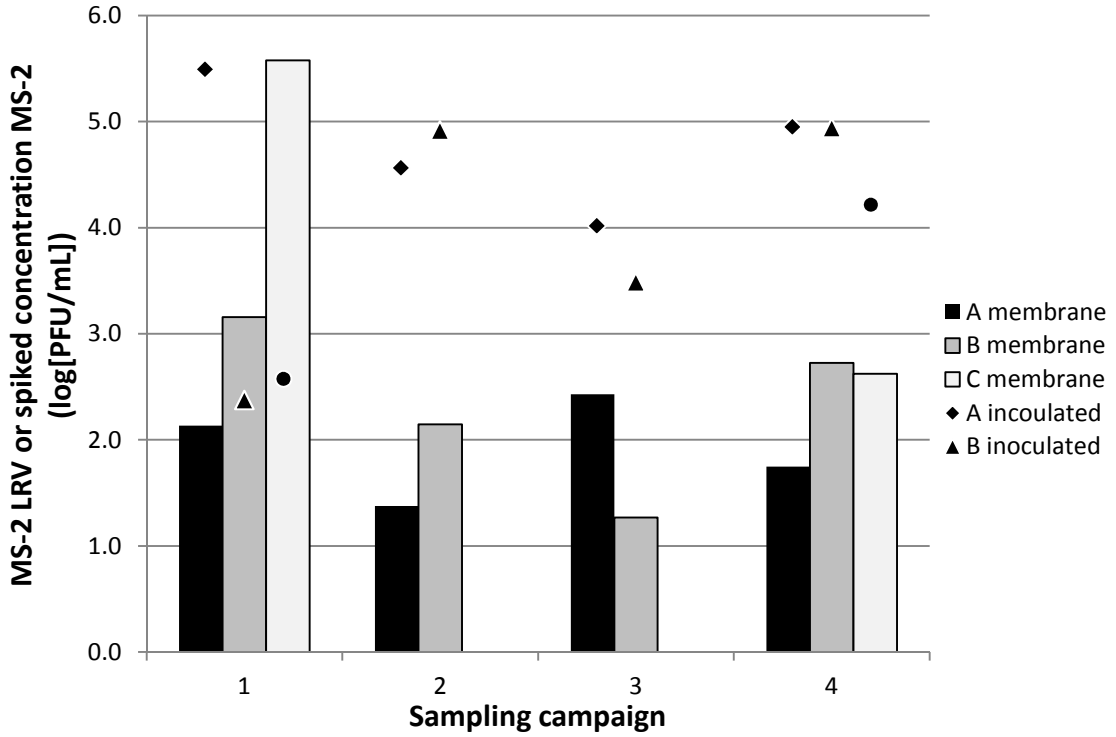

Figure 5.4. LRVs (bars) and spiked concentration (dots) of MS-2 of the three membrane modules tested in the four challenge test trials performed. Black bars correspond to A membrane, grey ones to B membrane and white ones to C membrane. Diamond, triangle and circle symbols correspond to the spiked concentration in each test to A, B and C membranes respectively.

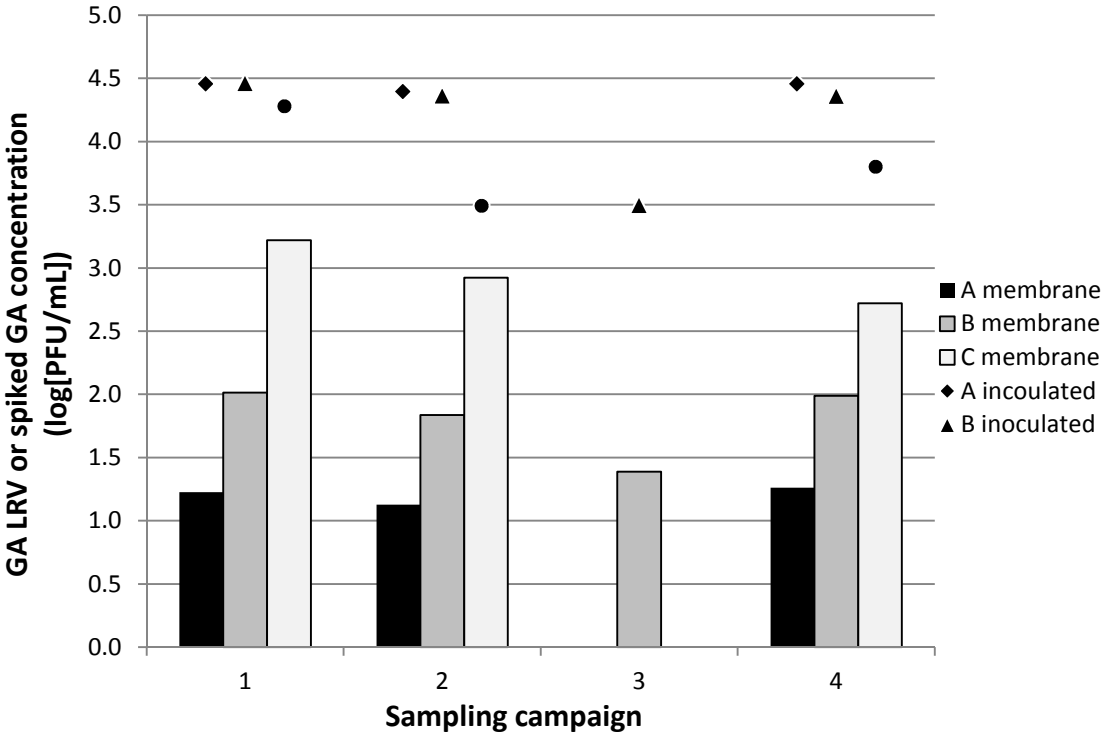

Figure 5.5. LRVs (bars) and spiked concentration (dots) of GA of the three membrane modules tested in the four challenge test trials performed. Black bars correspond to A membrane, grey

ones to B membrane and white ones to C membrane. Diamond, triangle and circle symbols correspond to the spiked concentration in each test to A, B and C membranes respectively.

5.3.3. Comparison of PDT and surrogates challenge tests

The PDTs performed before each challenge test in the three UF membranes did not detect any integrity failure during the four campaigns conducted (i.e. pressure drop experienced was lower than the threshold which alerts of potential fibres impairment, which was defined by membrane manufacturers).

As commented previously, PDT provides information on membrane integrity, even though there is a certain discrepancy between the results obtained from the pressure decay values and the surrogate inoculation and removal quantification by analysing feed and permeate streams. Qualitative PDT, based on checking if the pressure decay during the test is below a certain value indicated by the membrane manufacturer, is also indicative of the system integrity. However, it is more limited since theoretical LRVs cannot be calculated (through Eq. 5.2). The most limiting feature of relying on PDT is the fact that defects smaller than 1 µm require pressures which cannot be held by low pressure membranes. Therefore, a certain defect size is required to be noticed in terms of pressure decay, which may mask impairments. Also, PDT accuracy is limited, since system failures (e.g. in valves and seals which do not necessary involve a permeate pollution) may result in false positives. On the other hand, PDT appears as an easy procedure to be implemented, which typically lasts less than 10-15 min, making it very attractive for water utilities when compared to other integrity tests. It has to be kept in mind that, in spite of its attractiveness, PDT requires stopping the production process.

The proposed challenge test with bacteriophages, especially PDR-1, and spores enabled a reliable assessment of the membrane integrity. Nonetheless, it required the system to temporally shutdown (typically 2-3 h) and to ensure a subsequent cleaning stage (even though the tested organisms were innocuous to human health). In order to avoid surrogates' aggregation, it was important to keep the spiked concentration within certain ranges, which might limit the maximum LRVs to be verified. Results could be obtained in 24h approximately and the associated analytical cost was low. Nonetheless, in the case of a DWTP dealing with feed water of relatively constant quality (pH, ionic strength) and low turbidity values, the bacteriophages could be spiked directly in the feed water and, thus, avoid the system stop. Similarly, in case the bacteriophages load in the feed water would be high, the seeding step could be eluded, avoiding the necessity to stop the production process.

5.4. Conclusions

The developed protocol was implemented successfully in the three existing hollow fibre UF configurations, enabling the performance of the test periodically.

PDR-1 and *Bacillus* spores rejections were above 4 $\log_{10}$. This indicated that the fibres of the three modules assessed were intact, because the surrogates sizes were well above the pore sizes assessed. These results were in accordance with the PDT outcomes, which enabled the detection of defects in the range of 1-3 µm with the applied pressures (1-2 bar). In the case of MS-2 and GA retention, differences were found between the different membranes and within the same one over time. In particular, MS-2 was typically removed to a larger extent. Probably this was due to the dissimilarities in hydrophobicity (GA > MS-2) and isoelectric point (MS-2 = 3.1 - 3.9; GA = 2.1 - 2.3 depending on the ionic strength of the suspension solution) (Langlet et al*.,* 2008). In this case, when the surrogates sizes were smaller than the membranes pore size, adsorption processes and electrostatic interactions played a significant role in viruses retention. As a result, the effect of fouling in the membrane as well as the membrane characteristics themselves, might explain the differences encountered.

Taking into account the data obtained during this work, the use of PDR-1 appeared as a suitable microorganism to assess membrane integrity because its size is slightly above the UF tested membranes pore sizes (20-40 nm larger), and *Bacillus* spores as a control (around 1 µm larger). As a result, the removal mechanism of these two surrogates relies on size exclusion, so that fibre impairment might lead to a lower retention. MS-2 and GA removals, due to their smaller sizes, mainly rely on adsorption processes and electrostatic interactions, so that they might be influenced by further factors, such as non-chemically removable fouling of the membrane, feed water characteristics, etc., which might imply a more difficult data interpretation. Nevertheless, this data could be used to comprehend membranes performance, besides the potential of providing membrane integrity information. Consequently, more challenge tests with the same membranes and for a longer period of time were conducted to obtain further conclusions in this direction (see Chapter 6).

The methodology proposed, with the three bacteriophages and *Bacillus* spores, can provide the operator not only with tools to determine the system integrity but also with information about the membrane status and hence, contribute to the understanding of its behaviour and enable the adaptation of the operational conditions accordingly. The implementation of this methodology could be beneficial to award removal credits to membrane based technologies, to undertake the direct testing in DWTP facilities and also in pilot testing studies, where pilot plants are exposed to extreme conditions, and hence, the validation of their removal pathogens rejection along time may be of utmost importance.

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CHAPTER 6

Direct ultrafiltration performance and membrane integrity monitoring by microbiological analysis

This chapter is based on:

Ferrer, O., Casas, S., Galvañ, C., Lucena, F., Bosch, A., Galofré, B., Mesa, J., Jofre, J., Bernat, X., 2015. Direct ultrafiltration performance and membrane integrity monitoring by microbiological analysis. Water Res., 83, 121-131.

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Abstract

The feasibility of substituting a conventional pre-treatment, consisting of dioxichlorination, coagulation / flocculation, settling and sand filtration, of a drinking water treatment plant (DWTP) by direct ultrafiltration (UF) was assessed from a microbiological standpoint, complementing the physico-chemical and operational evaluations performed previously (Chapter 3 and 4). Bacterial indicators, viral indicators and human viruses were monitored in raw river, ultrafiltered and conventionally pre-treated water samples during two years. Direct UF proved to remove bacterial indicators quite efficiently and to a greater extent than the conventional process did. Nevertheless, the removal of small viruses such as some small bacteriophages and human viruses (e.g. enteroviruses and noroviruses) was lower than the current conventional pre-treatment.

Due to the challenging scheme direct UF represented from a membrane integrity standpoint, and the importance of the latter to guarantee the membrane removal capacity, its impairment was monitored during 2 years. Indeed, membrane integrity was conducted periodically by means of the tailored tests based on bacteriophages with different properties (MS-2, GA and PDR-1) and bacterial spores (*Bacillus* spores) previously designed (Chapter 5). Membrane integrity was not compromised despite the harsh conditions faced by directly treating raw river water. Bacteriophage PDR-1 appeared as a suitable microbe to test membrane integrity, as its size is slightly larger than the considered membrane pore size. However, its implementation at full scale plant is still challenging due to difficulties in obtaining enough phages for its seeding.

6.1. Background

The limited fraction of water suitable for human consumption together with the increasing population and water demand leads to the need of using alternative water resources, sometimes of compromised quality. Among the factors related to the use of challenging water resources, over a hundred of different pathogenic waterborne organisms including protozoa, bacteria and viruses have been identified as a topic of concern for drinking water production (Hunter, 1997). As a result, the use of advanced technologies, among them membrane filtration processes, has gained increasing attention. In particular, low pressure membrane systems have experienced an increase, almost exponential, in globally installed volume (Gimbel et al., 2003), with 60% of its applications in the drinking water treatment sector (David et al., 2008).

Low pressure membranes (microfiltration (MF) and ultrafiltration (UF)) retain suspended solids and microbes greater than their pore size by size exclusion mechanisms. Bacteria and protozoa are in general highly retained by membrane processes (Jacangelo et al., 1997). Loose of membrane integrity could enable the passage of those microorganisms or compounds greater than its nominal pore size, resulting in compromised water quality. Several reasons can cause the failure of membrane fibres (Guo et al., 2010): chemical corrosion, incorrect installation and maintenance, inappropriate operation conditions causing stress and strain and impairment by objects not removed in the pre-treatment. Nevertheless, membrane operation can also potentially increase membrane performance: membranes pore clogging could result in an apparent tighter pores size distribution, enhancing the removal by sieving effect.

Besides size exclusion, adsorption and electrostatic interactions can also lead to a certain rejection of compounds and microbes smaller than the pore size. In the case of UF only some viruses are minor than the pore size of the membranes (EPA, 2003). Adsorption of viruses smaller than the membrane pore size depends on the nature of the membranes (Sobsey and Glass, 1984, Herath et al., 1999, von Voorthnizen et al., 2001), the water characteristics such as ionic strength, organic matter content, etc. (Sobsey and Glass, 1984, Herath et al. 1999, Langlet et al., 2009), the coating of the membrane with adsorbed, mostly organic, matter or the biofilm formation (Ueda and Horan, Farahbakhsh and Smith, 2004, Marti et al. 2011) and the viruses themselves (Langlet et al., 2008, 2009, Michen and Graule, 2010, Goodridge et al., 2004). Therefore, regarding virus retention, all these factors entail low pressure membranes becoming a barrier with potentially changing efficiency, even in the case that the membrane remains intact and the quality of water to be filtered is kept constant.

The efficiency of a membrane regarding the retention of viruses can be assessed either with the human viruses themselves or with bacteriophages used as surrogate viral indicators (IAWPRC Study Group, 1991, Jofre, 2007, Lucena and Jofre, 2010). Human viruses are relatively scarce in potential water resources and their seeding in experiments is not recommended for sanitary reasons and it is hardly feasible when great volumes of water are tested (e.g. in pilot/full scale installations). On the other hand, naturally occurring bacteriophages used as indicators of human viruses, such as somatic coliphages and F-specific RNA bacteriophages

(IAWPRC Study Group, 1991) can be used to monitor the performance of a given membrane system (USEPA, 2001, IAWPRC Study Group, 1991). Due to the characteristics of certain bacteriophages (different sizes, different surface properties, easiness to grow large concentrations in the laboratory) they appear as appropriate to conduct membrane integrity tests. As an example, MS-2, sized 20 - 25 nm, is recommended by USEPA for the assessment of integrity of reverse osmosis (RO) membranes (NSF-EPA, 2011).

Alternative drinking water treatment schemes need to demonstrate their physico-chemical and microbiological removal capacity. Direct UF has proven its capacity to substitute DWTPs conventional pre-treatment from a physico-chemical and an operational standpoint, using full scale modules and continuously dealing with challenging surface water (Ferrer et al., 2013a, Galvañ et al., 2014, Briceño et al., 2014). An advantage of this configuration is its microbiological removal capacity which does not require chemical disinfectants. Nevertheless, up to the moment it has not been fully characterised using bacteria, bacteriophages and human viruses simultaneously. Taking into account that direct UF relies solely in a single membrane filtration step and that it would replace an initial disinfection and coagulation/flocculation and settling, which are the stages that remove microbes to a significant extent within a DWTP (WHO, 2004), it becomes necessary to study in detail its long term removal capacity to protect public health from microbial risk. Hence, this work compared the performance of direct UF with conventional pre-treatment from a microbiological standpoint, analysing traditional bacterial indicators (*E. coli* and spores of sulphite reducing clostridia (SSRC)), viral indicators (somatic coliphages and F-specific RNA bacteriophages) and human viruses (culturable enteroviruses measured as plaque forming units (PFUs) on BGM cells, and genome copies (GC) of enteroviruses (22 - 25 nm) and genotypes I and II of noroviruses (27 - 38 nm)) during two years.

Membrane integrity is of utmost importance to guarantee its removal capacity, especially in the treatment scheme considered here (direct UF). The best process indicator in terms of virus removal currently is challenge testing with MS-2 bacteriophage (Antony et al., 2012). However, other surrogates for virus removal such as Qβ are also being used (Matsui et al., 2003, Matsushita et al., 2005, Otaki et al., 1998, Shirasaki et al., 2007, Urase et al., 1996), but at bench scale. Langlet et al. (2009) quantified lower removal rates of Qβ than MS-2 and suggested it as a better candidate to determine membrane virus removal in worst case scenarios. Taking into account that virus rejection depends on several parameters related to the membrane and the feed water characteristics as well as the microbe itself, there is a need to determine the suitability of different organisms for microbes integrity testing as well as to validate it with full scale modules over a long period of time with real water. Indeed, there is limited information on ageing effect on pathogen removal (Antony et al., 2012). This work compared bacteriophages MS-2 (22 nm) and GA (22 nm), both smaller than the membrane nominal pore size (40 nm) but differing in surface charge and hydrophobicity, PDR-1 (60 - 70 nm) bacteriophage, slightly greater than the pores, and *Bacillus* sp. spores (length >1,000 nm; diameter > 500 nm) much greater than the membrane pores. As a result, surrogates with different properties and hence, potentially different behaviour, were considered, providing information on membrane integrity and virus removal. Additionally, their rejection was compared to physico-chemical indicators (turbidity and UV_{254}) to determine if those

parameters, easier to measure, could provide equivalent information. Finally, these tests were conducted during two years to monitor membrane integrity of the direct UF membrane, to identify whereas changes occurred due to fouling or ageing. Long term studies (2 years) at pilot scale dealing with real water, assessing both naturally occurring and spiked microorganisms, with low detection limits, if existing, are scarce.

6.2. Materials and methods

6.2.1. Case study and experimental set up

The case study selected was Sant Joan Despí Drinking Water Treatment Plant (SJD DWTP), located in the vicinities of Barcelona (Spain), which treats Llobregat River water to provide drinking water almost to 50% of the population of the Metropolitan Area of Barcelona, equivalent to approximately 1.5 million inhabitants (CETaqua and Fife-Schaw, 2010). The Llobregat River presents a typical Mediterranean character, representing a challenging water source due to its high variability in terms of water quality and quantity. The SJD DWTP is a complex multistep treatment that combines a conventional pre-treatment, consisting of an oxidation with chlorine dioxide, coagulation-flocculation, settling and sand filtration, followed by either ozonation and activated carbon filtration or by UF and RO with a final post chlorination step. In this study, the results of a prototype plant consisting on direct UF of Llobregat River raw water were compared to the results achieved by the current initial steps of SJD DWTP in terms of microbiological content removal, to assess its capacity to substitute the existing conventional pre-treatment (dioxichlorination, coagulation/flocculation (with aluminium salts), settling and sand filtration).

The direct UF prototype, of 15 m^3/h nominal capacity, consisted of a strainer (1 mm) and a coagulation tank with a stirrer, used when coagulation with ferric chloride was needed, submerged outside-in polyvinylidene difluoride (PVDF) membranes (1 membrane cassette with 10 Zeeweed® 500D modules) contained in a 8,000L feed tank, pumping systems, reservoirs, dosing and sampling points, as well as an automatic control and data acquisition system. The nominal pore size of the membranes installed was 40 nm, and the internal and external fibres diameter 0.8 mm and 1.99 mm, respectively. The prototype operated continuously since May 2011 until July 2013 facing very different scenarios of Llobregat River water quality (e.g. turbidity ranging from 8 up to > 1,000 NTU). Further details of the prototype and its operation optimisation can be found in Galvañ et al. (2014).

The sampling campaigns were conducted simultaneously in the direct UF prototype and in the conventional pre-treatment in order to obtain comparable results. Membrane integrity tests were only performed in the direct UF prototype. Sampling points were raw river water (Llobregat River), prototype permeate and sand filtered water (Figure 6.1). The sampling frequency depended on the test: bacterial indicators analyses once or twice a month and virus analyses and membrane integrity tests every 3-4 months, during two years.

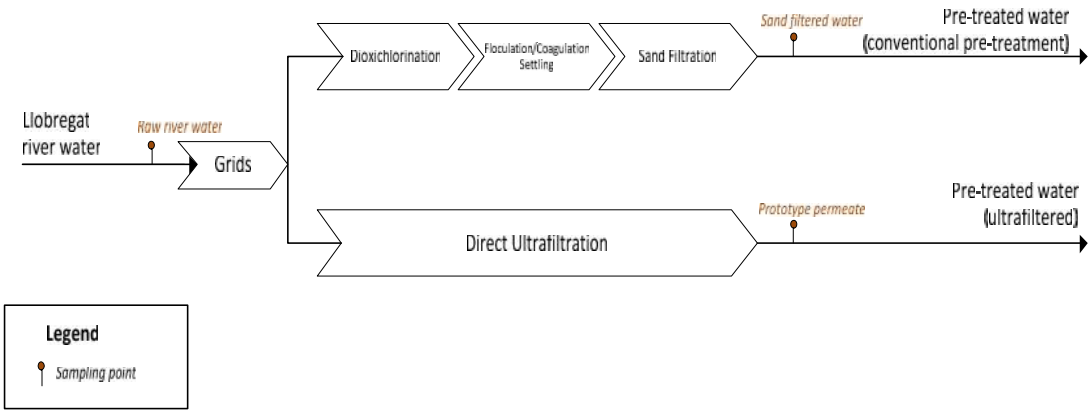

Figure 6.1. Direct UF and conventional pre-treatment schemes compared within this study.

6.2.2. Membrane integrity tests seeding stocks preparation and tests performance

Highly concentrated stocks of phages MS-2 and GA were obtained on host strain *Salmonella thyphimurium* WG49 according to ISO (1995) and stored at -80ºC in 20% glycerol until use.

PRD-1 stocks were obtained on *E. coli* MS1000. For such purpose, PRD-1 phages were plated with 3 mL of top agar (ISO, 2000) and 0.2 mL of an *E. coli* MS1000 overnight culture and were incubated at 37ºC. After 24 hours, the phage lysate was re-suspended in 4 mL of peptone saline solution (ISO, 1995) and centrifuged at 3,000 rpm for 10 minutes. The supernatant was filtered through a 0.22 µm pore size low protein binding polyethersulfone membrane filter (Millipore, Bedford, MA) and stored at -80ºC in 20% glycerol until use.

Bacillus sp spores were obtained by feed-batch fermentation in a 10 L bioreactor with glucose and acid hydrolysed casein as the main nutrients. The culture was left to grow and to produce spores during 72 hours. Spore making was determined by phase contrast microscopy. Then the culture was harvested and centrifuged in a GEA Westfalia Separator disc stack centrifuge up to 8,000 x *g* at 20ºC. The cell/spore concentrated were centrifuged, pelleted and washed three times in Ringer solution at 12,000 x *g* at 4ºC. The final pellet was re-suspended in a final volume of 1,200 mL and distributed in containers holding 50 mL, which were treated at 80±1ºC during 60 min to eliminate vegetative cells. The spore content of the suspensions ranged from $1.6E^{+9}$ to $5.3E^{+10}$ spores per mL and diluted to contain about $1E^{+10}$ spores per mL, since greater concentrations generated a lot of aggregation among spores. The suspensions were kept at 4ºC until use.

The protocol used to conduct the membrane integrity test was the one described in Ferrer et al. (2013b). Initially, a chemically enhanced backwash (CEB), under the conditions recommended by the membrane manufacturer, was conducted and afterwards the feed tank was drained and manually cleaned. Then, it was filled with 8,000 L approximately of drinking water and it was conditioned with sodium thiosulfate (JT. Baker, 1N, Analyzed Grade) to remove any potential free chlorine presence, and sodium chloride (JT. Baker, ACS grade) to achieve 2,000 µS/cm, to keep constant the ionic strength of the solution. The prototype filtered at 24.5 L/(m^2·h) (LMH) during 2 minutes to flush the pipes and to measure the

membrane permeability before the test (to quantify the extent of membrane fouling not removable by chemical means). Subsequently, the test microorganisms were spiked into the membranes tank by pairs in the following way: one with phages MS-2 and PDR-1 and the other with GA phage and *Bacillus* spores. For each indicator, 1 mL of a high title suspension ($1E^{+10}$ or greater indicator per mL, aiming at ensuring between $1E^{+3}$ and $1E^{+4}$ Plaque Forming Units (PFUs) or Colony Forming Units (CFUs) per mL in the feed tank) was diluted in 1L of feed water. After thorough agitation, a 5 mL aliquot was taken to count the indicators seeded and the rest was poured to the membranes tank. Subsequently the water in the membranes tank was meticulously agitated during 45 min. Afterwards, filtration started at 24.5 LMH and after 2, 4, and 6 min both the membranes tank (i.e. feed) and the permeate were sampled simultaneously. The microorganisms spiked in each integrity testing experiment were counted in 1 mL of the feed sample and in the case of the permeate in 1 L for bacteriophages and 10 mL for spores, according with the protocols described ahead.

6.2.3. Virus quantification

Enteroviruses (ENT) and noroviruses (NOR) in 1 L of raw river water were concentrated by organic flocculation, adding 3% of beef extract (BBL-Becton Dickinson, Sparks, MD) and adjusting the pH to 3.5 as described by Katzenelson et al. (1976).

Enteroviruses and noroviruses in pre-treated water (both direct UF permeate and dioxichlorinated, coagulated/flocculated and sand filtered samples) were concentrated by adsorption to and elution from positive charged cartridge filters MK-100 (AMF Corp., CUNO, Meriden, CT). For such purpose, 1,000 L were filtered through MK cartridges. Viruses were eluted with 0.25 M glycine buffer solution at pH 10.5 for 25 min. A secondary concentration step was conducted by organic flocculation, adding 3% of beef extract (BBLBecton Dickinson, Sparks, MD) and adjusting the pH to 3.5 as described by Katzenelson et al. (1976). Prior to infection of the BGM cells, the concentrates were decontaminated and detoxified by filtration through 0.22 mm pore size low protein binding polyethersulphone membrane filters (Millipore, Bedford, MA).

Buffalo green monkey kidney cell line (ECAAC 90092601) was used for the enumeration infectious enteroviruses (ENT1). The method used for determination of PFUs was the double-layer plaque assay according to Mocé-Llivina et al. (2004). Detection limit was 0.2 PFU/L.

To quantify the genome copies (GC) of enteroviruses (ENT2), viruses in the concentrates described above were further concentrated and purified as described elsewhere (Hundesa et al., 2009, Puig et al., 1994). For the one-step quantitative real time polymerase chain reaction (RT-PCR) method a set of primers and Taqman probe targeting a 155 bp of the 5` untranscribed enteroviral genome region was used. The primers and probe sequences used to amplify and to detect viral genomes are described in Hwang *et al*. (2007) and Nijhuis et al. (2002), respectively. Briefly, the RT-PCR reaction was carried out in a total volume of 25 µL of nucleic acids extracted using a QIAamp viral RNA extraction kit (Qiagen, Madrid, Spain). The limit of detection of the technique was 35 Genome Copies (GC)/L of raw river water and sand filtered water and 0.75 GC/L in the ultrafiltered samples. Values in the detection limit were

350 GC/L in raw river and sand filtered samples and 50 GC/L in the ultrafiltered ones. In this case, values were calculated provided that 1,000 L had been filtered.

To determine noroviruses GC, a standardized one-step real-time TaqMan RT-PCR using previously described primers and probes was employed for the detection of human noroviruses (NoVs) of genotype I (GI) (NoV GI) (da Silva et al., 2007, Svraka et al., 2007) and genotype II (GII) (NoV GII) (Kageyama et al., 2003, Loisy et al., 2005) as previously described by Pérez-Sautu et al. (2012). Virus/nucleic acid extraction and enzyme efficiencies were monitored as described elsewhere (Le Guyader et al., 2009), and used to estimate the actual genome copy numbers from the raw genome numbers measured by real-time RT-PCR in duplicate. The limit of detection was 16 GC/L of raw river water and sand filtered water and 0.8 GC/L in the ultrafiltered ones. In this case, values were calculated provided that 1,000 L had been filtered.

6.2.4. Bacterial indicators quantification

Escherichia coli were enumerated by membrane filtration using Chromocult® coliform agar (Merck, Germany) supplemented with antibiotics (*E. coli*/coliform selective supplement; Merck, Germany). Spores of sulphite-reducing clostridia (SSRC) were determined according to Bufton (1959). Spores of *Bacillus* sp in 10 mL aliquots of the samples were enumerated by pour plate technique using an adapted *Bacillus* specific medium (Yeast extract 20 g, acid-hydrolysed casein 2 g, agar 15 g. distilled H_2O_2 1,000 mL) after a thermal shock at 80 ºC during 10 minutes. Plates were incubated at 30 ºC during 48 to 72±3 h. One hundred mL were examined for the three bacteria studied in all types of samples; therefore the detection limit was 10 CFUs/L.

6.2.5. Bacteriophages quantification

Samples with expected low virus content were concentrated from 1 L of the water sample according to the method described by Mendez et al. (2004).

Plaque forming units (PFUs) of bacteriophages were counted after filtration of the sample through 0.22 mm pore size low protein binding polyethersulphone membrane filters (Millipore, Bedford, MA), and the phages were analysed by the double agar layer technique. Somatic coliphages (SOMCPH) were enumerated on host strain *E. coli* WG5 in accordance with the standardized procedure (ISO, 2000) and F-specific RNA bacteriophages (FRNAPH), as well as bacteriophages MS-2 and GA on host strain *Salmonella thyphimurium* WG49 according to ISO (1995). Bacteriophage PRD-1 was also enumerated by the double layer agar technique on strain *E. coli* MS1000 according to the procedures standardised for somatic coliphages (ISO, 2000). The volumes tested for bacteriophages in the different kinds of samples set up the detection limit at 1 PFU/L.

6.2.6. Physico-chemical parameters quantification

Both Llobregat River water and UF membrane permeate were characterised physico-chemically in a routine basis. The parameters monitored and the methods used were: turbidity by nephelometry (WTW GmbH VisoTurb 700IQ), total suspended solids (TSS) by ESS 340.2, absorbance at 254nm (UV_{254}) by spectrophotometry (Hach-Lange DR 5000), silt density index (SDI_{15}) and modified fouling index ($MFI_{0.45}$) by ASTM D4189 (Simple SDI Meter 9C-281-0157) and dissolved organic carbon (DOC) by combustion-infrared method using a DOC analyser (non-purgeable organic carbon, UNE-EN 1484), after filtration with a 1.2µm glass fibre filter for the raw water samples (TOC-V CSH Shimadzu). When conducting membrane integrity tests, turbidity and UV_{254} were measured from feed and permeate samples (both unfiltered and filtered by 0.45µm glass fibre filter in the case of the feed samples, and unfiltered for the permeate).

6.2.7. Data treatment

Logarithmic removal values (LRVs) were used to calculate the performance of the processes considered, calculated as shown in Eq. 6.1, being C_f the microorganism concentration in the feed stream and C_p the concentration in the permeate.

$$LRV = \log\left(\frac{Cf}{Cp}\right) \qquad \text{Eq. 6.1}$$

The software SPSS version 14.0 (SPSS Inc., Chicago, IL) was used to conduct the statistical analyses. Concentration values below the detection limit were taken as the detection limit for statistical analysis. This leads to calculate reductions equal or smaller than the actual reported values. For actual 0 values, the value 1 was used to calculate the logarithm. Differences were considered as significant at $P \leq 0.05$, as defined by the ANOVA or the Kursal-Wallis test.

Uncertainty analyses on the recovery of the assessed microorganisms were not conducted, although works addressing this issue can be found in literature (Wu et al., 2013).

6.3. Results and discussion

6.3.1. Llobregat River water characterisation

Human viruses, bacteria and bacteriophages concentrations from the Llobregat River are reported in Table 6.1. The concentration of bacterial indicators in the studied sector of the Llobregat River were within the same order of magnitude than those of rivers of surrounding countries downstream of densely populated areas (Briancesco and Bonadonna, 2005, Cabral and Marques, 2006, Petit et al., 2001). Values missing were due to incidences in the testing procedure.

All the naturally occurring indicators considered were detected in all the samples with average values of *E. coli*, spores of sulphite reducing clostridia (SSRC) and somatic coliphages (SOMCPH) between 4.19 and 4.48 log_{10} units/L, and F-specific RNA bacteriophages (FRNAPH) averaging 1 log_{10} unit lesser. The values reported were similar to data previously published for the same Llobregat River section (Rubiano et al., 2012).

As shown in Figure 6.2, only one value deviated more than 3-fold the standard variation of the data set. With the exception of this outlier value, all the other values were in between ±3σ limits so that meaningful variations were not identified in the feed water quality regarding microbial indicators with the sampling campaigns conducted. Although it appeared that there was a certain increase in the concentrations of the bacterial and viral indicators in the second half of the sampling period, the difference was not significant (ANOVA, $P > 0.05$) for any of the indicators considered.

In terms of human viruses, infectious enteroviruses (ENT1) were only found in 1 of 7 samples tested, which was similar to what had been described in Rubiano et al. (2012). In contrast, genomes copies (ENT2, NoV GI and NoV GII) were detected by q-RT-PCR in all samples tested. Values in CG log_{10} units/L ranged from 3.30 to 5.77 for enteroviruses and from 2.90 to 6.03 and from 3.13 to 5.82 for noroviruses genotype I and II respectively. Values for noroviruses were comparable to those described previously in the same river section (Pérez-Sautu et al., 2012). No previous values of GC of enteroviruses are available for the Llobregat River but the concentrations determined were comparable to the ones found in river water samples collected in France with concentrations of *E. coli* similar to the ones reported herein (Schvoerer et al., 2001).

Table 6.1. Concentrations of bacterial and viral indicators and human viruses expressed in log_{10} units per litre of raw river water sample. Units are CFUs for *E. coli* and SSRC; PFUs for SOMCPH, and FRNAPH and ENT1; and GC for ENT2, NoV GI and NoV GII.

	Positive samples	***Mean* (log_{10}unit/L)**	**Standard deviation (log_{10}unit/L)**	**Minimum (log_{10}unit/L)**	**Maximum (log_{10}unit/L)**
Indicator					
E. coli (CFU)	46/46	4.28	0.49	3.00	5.71
SSRC (CFU)	47/47	4.19	0.35	3.48	5.10
SOMCPH (PFU)	47/47	4.48	0.37	3.81	5.54
FRNAPH (PFU)	46/46	3.15	0.66	2.30	4.56
Virus					
ENT1 (PFU)	1/7	-	-	< 0.20	0.62
ENT2 (GC)	6/6	4.69	0.86	3.30	5.77
NoV GI (GC)	6/6	4.20	1.63	2.90	6.03
NoV GII (GC)	7/7	4.65	1.09	3.13	5.82

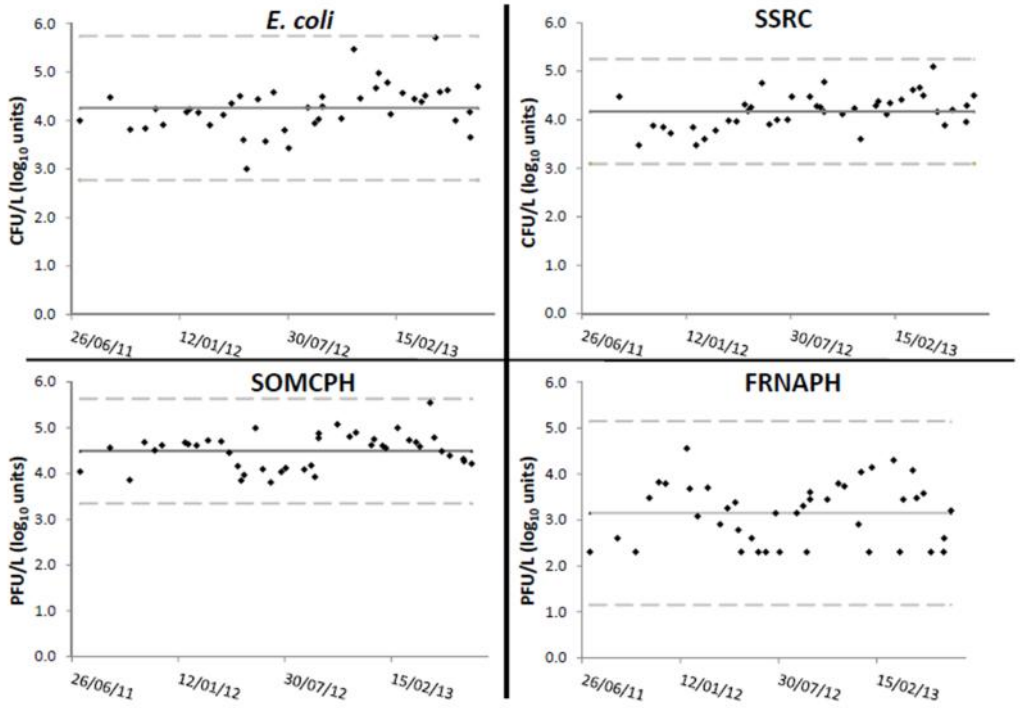

Figure 6.2. Concentration evolution along time of *E. coli*, SSRC, SOMCPH and FRNAPH in the river water samples. Centre line corresponds to the data mean, and the upper and lower line to the mean ±3σ standard error, respectively.

The Llobregat River physico-chemical parameters for the considered period are summarised in Table 6.2. Despite the variability of the raw river water, the quality of the permeate produced within the direct UF scheme was stable, with turbidities consistently below 0.09 NTU and TSS under 1.0 mg/L. Taking into account the high inlet turbidity changeability (8 - >1,000 NTU), the low variability of the UF permeate demonstrated the reliability of the process in terms of physico-chemical parameters, being independent of feed water quality. The average removal rates for turbidity, TSS, UV_{254} and DOC were 99.4±0.1%, 97.1±1.1%; 15.31±2.06% and 16.94±4.81% (confidence level of 0.05), respectively for the direct UF scheme. Further details of the prototype performance from a hydraulic and physico-chemical point of view can be found in Galvañ et al. (2014).

Table 6.2. Average ± confidence interval (significance of 0.05) of the Llobregat River and UF permeate physico-chemical parameters assessed during May 2011 – July 2013. HL: high level (i.e. more than 5%/min).

Parameter	Unit	Raw river water	UF permeate water
Turbidity	NTU	169.3 ± 61.9	0.08 ± 0.005
TSS	mg/L	153.03 ± 58.72	0.84 ± 0.14
UV_{254}	cm^{-1}	0.1105 ± 0.0075	0.0861 ± 0.0025
DOC	mg/L	6.19 ± 1.30	4.03 ± 0.26
SUVA	L/(cm·mg)	2.34 ± 0.21	2.21 ± 0.08
SDI_{15}	%/min	HL	1.76 ± 0.44
$MFI_{0.45}$	s/L^2	2,534.5 ± 522.1	0.37± 0.44

6.3.2. Microbial elimination by direct ultrafiltration and conventional pre-treatment

i) Indicator pathogens presence in the treated water

Presence and numbers of indicators and human viruses in the conventional pre-treated (dioxichlorination, coagulation/flocculation, settling and sand filtration) water are listed in Table 6.3 and its evolution along time is plotted in Figure 6.3. Both bacterial and viral indicators were found in a number of samples ranging from 5 out of 34 for FRNAPH (the less abundant) and 28 out of 35 for SSRC (the most abundant). Maximum values ranged from 0.85 $\log_{10}$ PFU/L for FRNAPH to 2.9 $\log_{10}$ CFU/L for SSRC.

Occurrence and concentrations of indicators and human viruses in ultrafiltered water are summarised in Table 6.4, and its evolution along time in Figure 6.4. Regarding bacterial indicators, *E. coli* was never found, whereas SSRC were found in 2 out of 40 samples, with a maximum value of 1.48 $\log_{10}$ CFU/L. Taking into account the larger size of bacterial indicators compared to the membrane pores, their removal would be expectable by sieving effect. Therefore, these results pointed out a good performance of the prototype in terms of removal of bacterial indicators, always greater than 500 nm, and hence, greater than the pore size of the UF membrane. Analogously to the physico-chemical parameters (Galvañ et al., 2014), a relationship between peak indicator concentrations in the ultrafiltered water and in the raw river water was not found. In contrast, bacteriophages, mostly somatic coliphages, were present in an important fraction (60%) of the direct UF samples, with a maximum value of 1.80 $\log_{10}$ PFU/L. F-specific RNA phages were present in 20% of the samples presenting a maximum value of 0.80 $\log_{10}$ PFU/L. Consequently, it could be concluded that a significant fraction of phages crossed the membrane. F-RNA are smaller (20 - 25 nm) than the pore size, whereas most of the coliphages are greater than 40 nm. However, a fraction of them, estimated to be between 1 and around 10% in sewage and river water samples (Muniesa et al. 1999) are *Microviridae* with a size of 20 - 25 nm and hence, similarly to F-RNA bacteriophages, are smaller than the pore size. This fraction was very likely to account for the SOMCPH that pass through the membrane.

The percentage of positive samples for SSRC was significantly greater (Krustal-Wallis tests, $P < 0.05$) in the sand filtered samples (Table 6.3) than in the ultrafiltered samples (Table 6.4). In the case of *E. coli* it was also greater but not significantly; probably the fact that all *E. coli* samples were negative and that the detection limit was used for the calculations influence this lack of significance. The percentage of positive samples for bacteriophages was slightly, but not significantly (Krustal-Wallis tests, $P < 0.05$), higher in the ultrafiltered samples; again this lack of significance may be due to the low number of positive samples and to the fact that the detection limit was used for the calculations. In the conventional pre-treatment, the removal of indicators was due to two processes: first, the removal caused by coagulation / flocculation - settling - sand filtration and secondly, the inactivation by chlorine dioxide. Then, it was not surprising that the SSRC that are known to be quite resistant to chemical disinfection (Venczel et al., 1997) were found in the sand filtered samples much more frequently than the other indicators. These results suggested that inactivation by chlorine (rather than the retention by sand filtration) played the most important role in the removal of indicators.

Some conventionally pre-treated water samples contained indicators, both bacterial and viral, whereas some ultrafiltered water samples contained bacteriophages but never bacterial indicators (Figure 6.3 and Figure 6.4, respectively). The treated samples containing indicators did not correspond to sampling days with greater indicators concentrations in river water. Therefore, the presence of indicators in treated water samples should be attributed to the treatments themselves and not to increased indicators concentrations in the river. Additionally, with the available data, no trend was observed in terms of indicator concentrations evolution along time in the treated samples from both processes.

Table 6.3. Concentrations of bacterial and viral indicators and human viruses expressed in log_{10} units per litre of treated water in the conventional pre-treatment scheme (dioxichlorination, coagulation/flocculation, settling, sand filtration). Units are CFUs for *E. coli* and SSRC, PFUs for SOMCPH, FRNAPH and ENT1, and GC for ENT2, NoV GI and NoV GII.

	Positive samples	*Mean (log_{10}unit/L)*	Standard deviation *(log_{10}unit/L)*	Minimum *(log_{10}unit/L)*	Maximum *(log_{10}unit/L)*
Indicator					
E. coli (CFU)	10/34	1.07	0.20	1.00	1.95
SSRC (CFU)	28/35	1.56	0.51	1.00	2.90
SOMCPH (PFU)	10/35	0.25	0.47	0.00	1.59
FRNAPH (PFU)	5/34	0.06	0.18	0.00	0.85
Virus					
ENT1 (PFU)	0/6	-	-	< 0.20	< 0.20
ENT2 (GC)	4/6	2.27	2.27	< 1.54	1.96
NoV GI (GC)	3/6	2.54	2.54	< 1.20	5.52
NoV GII (GC)	3/6	2.22	2.22	< 1.20	4.95

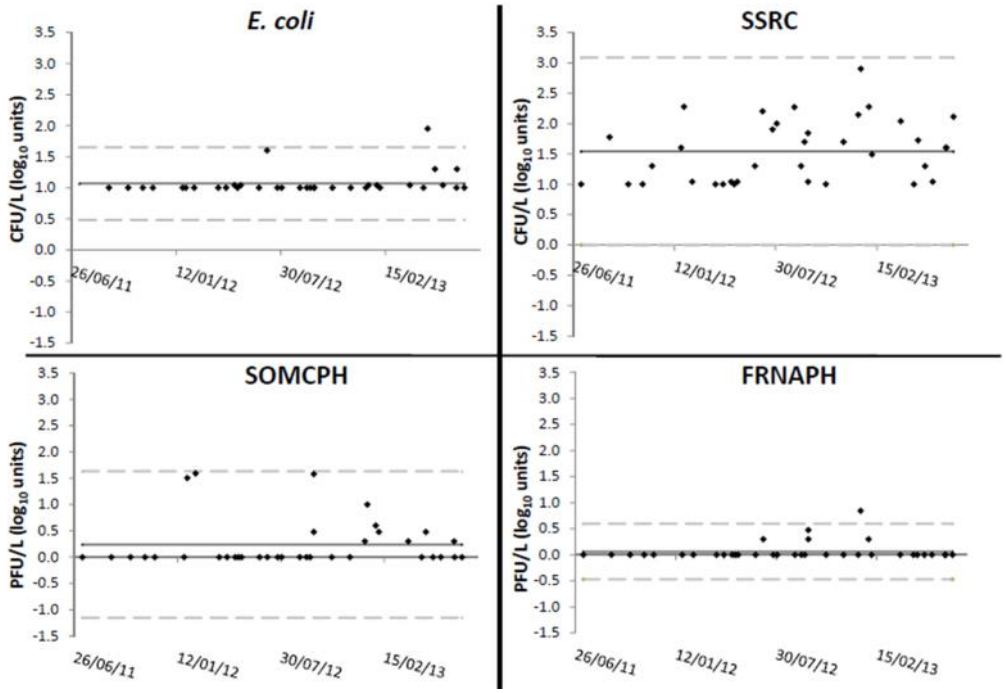

Figure 6.3. Concentration evolution along time of *E. coli*, SSRC, somatic coliphages SOMCPH and FRNAPH in in pre-treated water samples with the dioxichlorination –

coagulation/flocculation-settling-sand filtration treatment scheme. Centre line corresponds to the data mean, and the upper and lower line to the mean ±3σ standard error, respectively.

Table 6.4. Concentrations of bacterial and viral indicators and human viruses expressed in log_{10} units per litre of ultrafiltered water. Units are CFUs for *E. coli* and SSRC, PFUs for SOMCPH, FRNAPH and ENT1, and GC for ENT2, NoV GI and NoV GII.

	Positive samples	*Mean (log_{10}unit/L)*	Standard deviation *(log_{10}unit/L)*	Minimum *(log_{10}unit/L)*	Maximum *(log_{10}unit/L)*
Indicator					
E. coli (CFU)	0/39	<1.00	0.00	<1.00	1.00
SSRC (CFU)	2/40	<1.01	0.07	<1.00	1.48
SOMCPH (PFU)	24/40	<0.55	0.52	<0.00	1.80
FRNAPH (PFU)	8/40	<0.08	0.18	<0.00	0.85
Virus					
ENT1 (PFU)	0/7	-	-	< 0.20	< 0.20
ENT2 (GC)	2/6	-	-	< 0.12	1.96
NoV GI (GC)	1/7	-	-	< 0.09	0.22
NoV GII (GC)	1/7	-	-	< 0.09	0.19

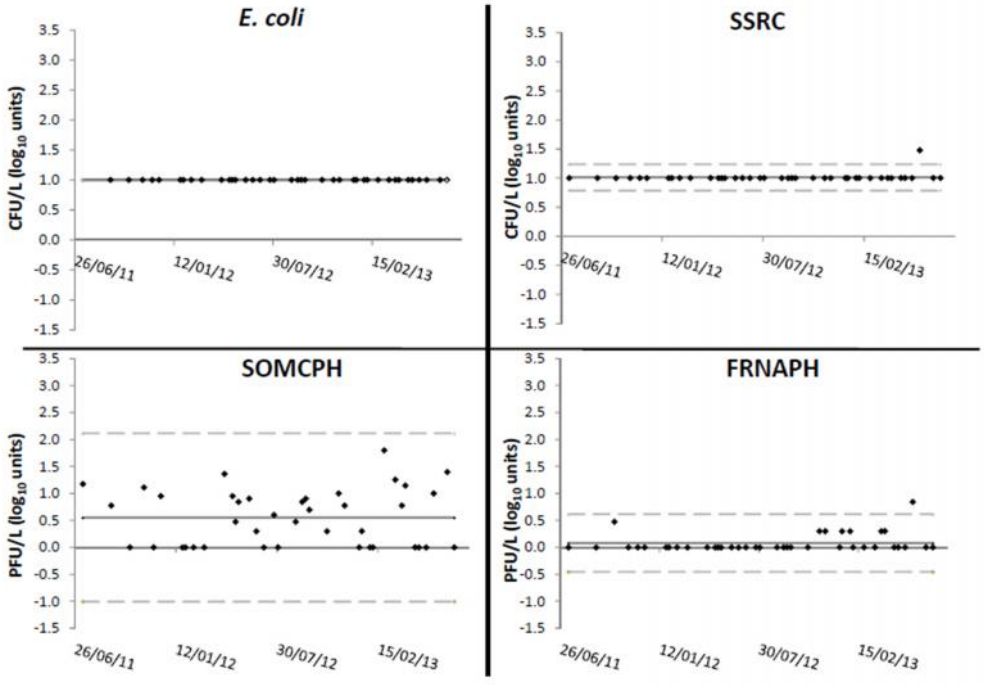

Figure 6.4. Concentration evolution along time of *E. coli*, SSRC, SOMCPH and FRNAPH in the ultrafiltered water (direct UF treatment scheme). Centre line corresponds to the data mean, and the upper and lower line to the mean ±3σ standard error, respectively.

No infectious enteroviruses (ENTPFU) were found either in the sand filtered water or in the ultrafiltered samples (Table 6.3 and Table 6.4). In contrast, CG of enteroviruses and noroviruses were present in half of the sand filtered samples. This was not unexpected since the q-RT-PCR had been described to poorly perceive the effects of disinfection processes: very

slight reductions were quantified by GC counts detected by PCR in comparison to those quantified by the infectious viruses (Sobsey et al., 1998, Simonet and Gantzer, 2006). Finding GC copies of a human virus in a given water sample does not mean that they pose a risk for human health (Gassilloud et al., 2003) because they may not be infectious. As a result, the infectious enterovirus and/or bacteriophage indicators measurement would be more appropriate than detecting genomes to assess the viral quality of the water for a DWTP when chemical or UV disinfection is included in the treatment process. Additionally, it is important to point out that these values corresponded to pre-treated water, still pending further treatment steps (e.g. RO) which fully guarantee the water quality distributed by SJD DWTP according to the existing legislation.

ii) Indicator pathogens reductions achieved by each treatment scheme

Figure 6.5 shows the average (±standard error) of the reductions achieved by the direct UF prototype and the conventional pre-treatment. As indicated in the methods section, the LRVs plotted were smaller than the actual ones, since the values used to calculate them were the detection values when detection was negative. Nevertheless, some conclusion could be drawn from these results. Average reductions of bacterial indicators achieved by the direct UF scheme were greater than 4 $\log_{10}$ units and those of viruses range from greater than 3 $\log_{10}$ units (FRNAPH) to greater than 3.9 (genome copies of Noroviruses II).

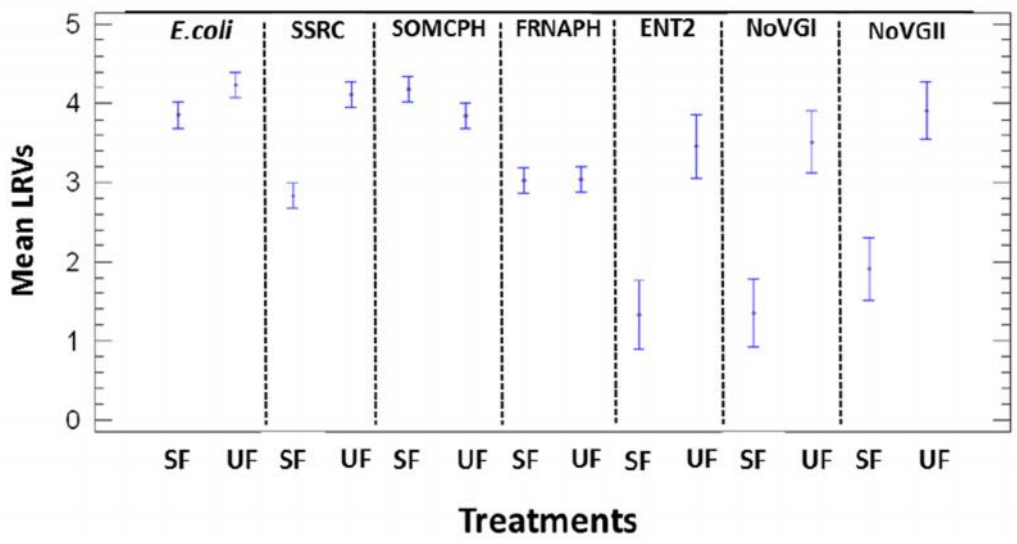

Figure 6.5. Mean LRVs of *E. coli*, SSRC, SOMCPH, FRNAPH, ENT2, NoV GI and NoV GII for direct UF (UF) and conventional pre-treatment (SF) schemes obtained during the two year period considered.

Regarding bacterial indicators, reductions achieved by direct UF were significantly (ANOVA, $P < 0.05$) greater than those attained by the conventional pre-treatment. In contrast, reductions of viral indicators were larger in the conventional pre-treatment. Though this was observed with both groups of bacteriophages only the reductions of SOMCPH achieved by the conventional pre-treatment were significantly (ANOVA, $P < 0.05$) superior than those achieved by direct UF.

In terms of human viruses genome copies (GC), the reductions achieved by direct UF were significantly (ANOVA, $P < 0.05$) greater than those achieved by the conventional pre-treatment, and similar (ANOVA, $P > 0.05$) to those achieved for bacteriophages by direct UF. These low reductions, less than 2 $\log_{10}$ units of GC of enteroviruses and noroviruses, could be due to the fact that GC counts detected by PCR use to experience very slight reductions when submitted to chemical disinfection in comparison to the decreases experienced by the infectious viruses (Sobsey et al., 1998, Simonet and Gantzer, 2006).

A relationship between the LRVs of any of the microorganisms considered within this project and the membranes transmembrane pressure (TMP), which was monitored when doing the microbiological sampling, was not found (data not shown). Nonetheless, the low number of positive microbiological samples and the fact that the detection limit was used to calculate the microbiological LRVs could mask the presence of such relationship, if existing.

6.3.3. Direct ultrafiltration membrane integrity tests

Seven experiments distributed evenly during two years were undertaken to assess the direct UF membrane integrity. The concentration of the seeding organisms were kept between $1E^{+3}$ – $1E^{+4}$ PFU/mL or CFU/mL for GA, MS-2 and *Bacillus* spores and between $1E^{+2}$ and $1.7E^{+3}$ PFU/mL for PDR-1 in the feed tank. Table 6.5 summarises the results obtained in terms of LRVs. No evident temporal trend was observed.

Table 6.5. LRVs of GA, MS-2, PDR-1 and *Bacillus* spores achieved during the membrane integrity monitoring experiments performed in the direct UF treatment scheme during a two year period.

Indicator	Positive detections in the permeate	LRV Mean	LRV St Dev.	LRV Minimum	LRV Maximum
GA	7/7	3.02	0.23	2.70	3.19
MS-2	7/7	2.81	0.31	2.34	2.81
PDR-1	6/7	> 5.00	1.24	3.69	> 6.22
Bacillus spores	2/7	> 5.10	1.05	3.86	> 5.89

As shown in Table 6.5, MS-2 and GA reductions were similar (ANOVA, $P>0.05$), flanking 3 $\log_{10}$ units. Since both bacteriophages are fairly smaller than the pore size, they were not expected to be retained by size exclusion, but by adsorption and static interactions. MS-2 and GA have been considered as extreme cases in terms of membranes absorbability, since they have different isoelectric point (MS-2: 3.1 - 3.9 and GA: 2.1 - 2.3) and hydrophobicity (GA > MS-2) (Langlet et al., 2008). Consequently, their use is considered to surrogate the behaviour of the great majority of human viruses. In conclusion, this set of experiments showed that concentrations of all the human viruses would be reduced by 3 $\log_{10}$ units by direct UF with a membrane like the one used in these experiments. These results were comparable to the LRV reported for naturally occurring bacteriophages analysed in the routine sampling campaigns reported herein and values published in literature (Zhu et al., 2005, Zodrow et al., 2009).

PDR-1 (60 nm in size) and *Bacillus* spores (length > 1,000 nm; diameter > 500 nm) removals were above 5 log_{10} units (Table 6.5), significantly different to the abovementioned bacteriophage rejections (ANOVA, P>0.05). These micro-organisms are removed by size exclusion. PDR-1 can go through the membrane either by the existence of pores greater than the nominal size or by failures in membrane integrity, whereas *Bacillus* spores only can go through by failures in membrane integrity. The presence of *Bacillus* spores in the permeate could be due to some environmental concentration because it has been reported that they are present in DWTP environments (Galofré et al., 2004). However, because the routine monitoring quantified some spores of *Clostridium* in the permeate and because LRVs of PDR-1 and *Bacillus* spores are similar, its presence in the permeate could be due to a small leakage in the UF system or some minor water by-pass in the prototype system.

The similarity between the LRVs of bacteriophage PDR-1 and *Bacillus* spores indicated that the pore size distribution of the membrane was within the average indicated by the supplier and that the fraction of pores greater than 60 nm was rather low or inexistent.

The LRVs calculated for the three bacteriophages and *Bacillus* spores did not diminish along the whole 2 year period. This indicated, on one hand that membrane integrity did not change, and on the other, that the properties of the membranes that affect the bacteriophages removal were not modified. As commented previously, besides size exclusion, adsorption and electrostatic interactions can also lead to virus/bacteriophages removal. Among the various factors already discussed that affect virus adsorption onto pores larger than their size, those related to feed water quality were kept constant during the assays performed thanks to the protocol defined and thus, only the ones related to membrane properties (e.g. irreversible fouling, structure, integrity, composition) could affect the results. The relationship between the bacteriophages and *Bacillus* spores removal during the integrity tests and the membrane TMP or the permeability divided by the pressure (temperature corrected) were assessed, but no relationship was observed (data not shown). As a result, it could be concluded that the membrane was not modified due to operation in such a way that its behaviour in terms of bacteriophages rejection had been altered, despite some irreversible fouling might have accumulated. This also indicated that the operation of the UF membrane during the 2 years period did not produce damages driving to a loss of integrity, despite the harsh conditions it faced in terms of water quality and continuous operation.

Finally, the comparison between the bacteriophages and the *Bacillus* spores LRVs with water physico-chemical parameters (data not shown of UV_{254} and turbidity measured during the integrity tests both in the feed and permeate) showed that these measurements cannot be used as surrogates of the UF membrane integrity tests based on microorganisms considered in this work. No relationship between their removal and the LRVs of GA, MS-2, PDR-1 or *Bacillus* spores was found, reinforcing the usefulness of these microbes, especially bacteriophage PRD-1, for membrane integrity tests targeting UF membranes whose pore sizes are greater than 20 nm.

6.4. Conclusions

Based on the results obtained in this work, it can be concluded that the direct UF scheme tested ensured the average removal of more than 5 $\log_{10}$ units of bacteria and viruses greater than 60 nm. In the case of microbes of this size, the performance of the assessed UF membrane significantly outperformed that of the dioxichlorination, coagulation/flocculation, settling and sand filtration pre-treatment, presenting greater removal values and lower variability. In contrast, the direct UF scheme only guaranteed a 3 $\log_{10}$ units removal of viral indicators and viruses smaller than 40 nm. For microbes of this size the performance of the dioxichlorination, coagulation/flocculation, settling and sand filtration (current pre-treatment) was better than that of direct UF membrane assessed (PVDF 40 nm in pore size), although not always significantly. According to the results obtained, the removal of the microbiological parameters assessed did not depend on their feed water concentration, analogously to the physico-chemical parameters assessed. Additionally, a relationship between the TMP and/or the permeability of the membrane and the human virus, bacterial and viral indicators rejection was not found, so that fouling effects on microbial performance were not observed within this work, which covered a two year period.

The implementation of direct UF proved to be a feasible alternative to conventional pre-treatment, being particularly advantageous regarding bacterial indicators and human viruses genome copies removal. As envisaged, the treatment of the Llobregat River water with direct UF would still require some further treatment to fully eliminate the viruses. However, in both cases, the current conventional pre-treatment and the direct UF scheme have / would have subsequent stages to ensure the final quality, fulfilling the drinking water quality standards. As a result, the substitution of DWTPs conventional pre-treatment would depend on several factors besides microbiological performance, such as space requirements, reagents dosage, waste generation and energy requirements, being the three first advantageous in the direct UF scheme, as described in complementary previous works (Galvañ et al., 2014).

The results presented here confirm other results regarding the usefulness of determining infectious virus to follow the effectivity of chemical disinfection processes compared to PCR genome copies, since not all genome copies are infectious and hence, represent a risk for human health.

Both naturally occurring viral indicators studied (somatic coliphages and F-specific RNA bacteriophages) were removed by direct UF similarly to human viruses when measured as GC, and similarly to seeded small bacteriophages (GA and MS-2). They can be suggested to be used to follow up the performance of UF membranes in terms of virus removal. Additionally, taking into consideration the large numbers found in the raw river water and in the permeate, as well as the straightforwardness of the standardised enumeration method (ISO, 2000), SOMCPH could be considered as a good tool for surveying the performance of UF membranes with indicators present in the raw river water. In this case, reductions between 3.0 and 4.0 $\log_{10}$ units of the numbers of somatic coliphages would be expectable.

A main concern related to membrane based processes is its ageing and the effects that this can provoke in terms of membrane integrity and thus, the quality of the permeate produced. The monitoring of the microbiological data obtained indicated that a perceptible loss of integrity of the tested membrane did not occur. This meant that dealing with raw river water directly of highly variable quality (turbidity ranging from 8 to >1,000 NTU) continuously during 2 years did not compromise the membrane (by physical and/or chemical means).

Bacteriophage PDR-1 and *Bacillus* spores appeared as suitable microbes to monitor membrane integrity. Bacteriophage PDR-1 is easier to grow to high densities than *Bacillus* and therefore it would be a better option than MS-2 and GA bacteriophages in some cases. However, obtaining sufficient amounts of phages to seed a full water treatment process is still challenging. Turbidity and UV_{254} measurements conducted during membrane integrity tests did not present a relationship with the microbes assessed during these tailored tests, so that they were not able to provide equivalent information within this work.

6.5. References

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CHAPTER 7

Reverse osmosis membrane degradation by chlorite, bisulphite, bromide and iron(III): effects on physico-chemical and transport properties

This chapter is based on:

Ferrer, O., Gibert, O., Cortina, J.L. (under review) Reverse osmosis membrane degradation by chlorite, bisulphite, bromide and iron(III): effects on physico-chemical and transport properties.

DOI:

Abstract

As discussed in previous chapters, the implementation of direct UF would encompass a significant reduction of reagents dosage within DWTPs, particularly in terms of chemical disinfectants and coagulants. This could have a positive impact on the reverse osmosis (RO) unit, since its performance can be deteriorated when exposed to certain chemicals. This chapter was devoted to RO membrane degradation by some compounds that would be avoided with the direct UF treatment scheme, extending therefore RO membrane lifetime.

The effects of a secondary oxidant (chlorite, linked to the dioxichlorination stage), a reducing agent (bisulphite, used to prevent RO membranes oxidation by chlorine based species), an halide ion (bromide, often present in water bodies) and a catalyst (iron(III), typically used as coagulant), separately and systematically mixed, on reverse osmosis (RO) membranes were assessed both in terms of membrane composition and performance. In the presence of chlorite and bromide, when iron(III) was dosed, a catalytic effect took place and bromine incorporation in the polyamide (PA) membrane active layer was around 10 fold greater than in absence of iron(III), probably due to hypobromous acid or bromine generation. This turned into a greater water permeation coefficient (1.2 fold compared to the virgin membrane) and an increase in chloride permeation coefficient (1.7 fold compared to the virgin membrane) without affecting rhodamine-WT (R-WT) passage under the conditions assessed. Chloride passage increase showed to be a time dependent process, with greater values under longer exposure time.

In the case of bisulphite exposure, when iron(III) was dosed an autooxidation of bisulphite occurred, probably generating free radicals which severely damaged the membrane, comprising a significant increase in chloride passage (chloride permeation coefficient was increased 5 fold compared to a virgin membrane under the conditions studied) rapidly. No major differences in terms of water permeability, R-WT passage and membrane composition were observed. Nevertheless, an increase in the size of the network pores, and a raise in the fraction of aggregate pores of the polyamide (PA) layer were identified, but no breakage of the amide bond was observed. These structural changes were therefore, in accordance with the transport properties observed.

7.1. Background

Reverse osmosis (RO) implementation has increased exponentially during the last decades due to its high rejection capacity (it rejects nearly all colloidal and dissolved matter (Fitzmann et al., 2007)) and its significant decrease in terms of energy requirements (Elimelech and Philip, 2011). Nowadays, one of the main challenges related to thin film composite (TFC) RO membranes is its integrity (Misdan et al., 2012). It is well known that certain oxidants such as free chlorine severely damage RO membranes and hence, membrane suppliers have already established maximum admissible concentrations to avoid membranes premature degradation (<0.1 mg/L of free chlorine, being 200-1000 mg/L·h the threshold above which eventual degradation may occur (Dow Process & Water Solutions)). Nevertheless, there may be other oxidants dosed and secondary oxidants that may be formed during the water treatment process that can degrade the RO membranes and encompass an undesirable performance, but have not been studied in detail yet. Additionally, raw water content and reagents used during water treatment itself may enhance membrane degradation processes, making its study more complex (Shemer and Semiat, 2011, Tessaro et al., 2005).

RO membranes are commonly TFC membranes consisting in a polyamide (PA) active layer (~50 – 250 nm thickness), supported by an asymmetric polysulfone support (~ 50 µm thickness) and a non-woven polyester fabric backing (~ 300 µm thickness) (Petersen, 1993). The partitioning-diffusion process which governs RO membranes water transport and solutes rejection takes place at the water-membrane interface (PA active layer) and across the membrane (Urama and Mariñas, 1997). The PA pore size distribution of RO membranes has been reported as bimodal, comprised of smaller and larger pores (Kim et al., 2005). The later, referred as aggregate pores, have been related to void space between polymer aggregates (Coronell et al., 2008) and their size has been estimated in 1.0 – 1.6 nm (Saenz de Jubera et al., 2012). The smaller ones, named network pores, have been associated to the interstitial space between polymer branches within an aggregate (Coronell et al., 2008) and their size has been estimated in 0.4 – 0.8 nm (Saenz de Jubera et al., 2012). A representation of network and aggregate pores is shown in Figure 7.1. Ionization behaviour of functional groups from the PA active layer, carboxylic and amine, has been modelled by acid-base equilibrium with the aqueous solution (Eq. 7.3, Coronell et al., 2008). Ion probing experiments combined with Rutherford Backscattering Spectroscopy (RBS) have enabled the quantification of the accessible deprotonated / protonated groups and thus, the determination of the associated acid-base parameters, providing insights into the pore size distribution, as well as other membrane properties like total concentration functional groups, degree of crosslinking, as shown in the work of Coronell et al. (2009).

The interaction of redox species compounds with the PA active layer can encompass morphological and chemical changes on the latter, which can result into alterations of the RO membrane separation properties. As a result, the quality of produced permeate can be compromised in an irreversible way, requiring the membrane replacement.

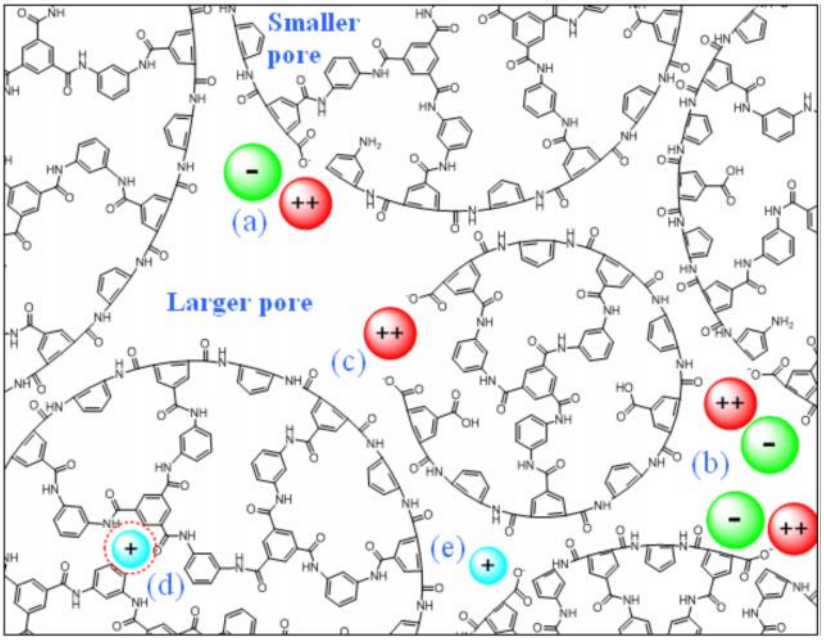

Figure 7.1. Sketch of aggregate and network pores of a PA membranes and interactions between ionized functional groups and counter ions. Source: Coronell et al. (2009).

As commented above, most PA based membranes are attacked by chlorine, eventually leading to impaired performance (Kwon et al., 2011). Despite there is not fully agreement in literature, it seems that chlorine compounds uptake by RO membranes can proceed mainly through three reaction pathways: i) N-chlorination, where the active chlorine species attack the unbonded electron pair of oxygen or nitrogen of the amide group; ii) direct ring chlorination, where an electrophilic attack on the PA aromatic ring is undertaken by active chlorine species; iii) Orton rearrangement, where a rapid N-chlorination is followed by an intramolecular rearrangement so that the chlorine migrates to the ring (Do et al., 2012a). Recently, Powell et al. (2012) concluded that, under acidic pH, N-chlorination followed by Orton rearrangement was more favoured, under neutral media, N-chlorination and Orton rearrangement occurred at a similar extent, and under alkaline environment, N-chlorination (and dechlorination of N-chlorinated amide links by hydroxyl ion) was more favoured. Morphologically, the uptake of chlorine has been attributed to transform PA crystalline regions into amorphous (not affecting the membrane performance at this stage) and afterwards, these amorphous regions are attacked by chlorine (da Silva et al., 2006, Antony et al., 2010, Kang et al., 2007, Avlonitis et al. 1992), deforming the polymer structure or causing depolymerisation through polyamide bond cleavage (Glater et al., 1994, Kwon et al., 2011). Chlorine uptake causes membrane performance decrease before amide link scission is detected (Powell et al., 2012). Different effects of chlorine exposure on RO membrane performance have been reported, both enhancing and deteriorating its performance, often linked to the pH under which the experiments were performed as well as the oxidant concentration and exposure time. Mitrouli et al. (2010) and Kwon and Leckie (2006a, 2006b) experienced an increase in water permeability at pH 9-10 and a decrease at pH 3-4, and an increase in salt passage in both acid and alkaline conditions after hypochlorite exposure. Similarly, Kang et al. (2007) noted a decrease in water flux and an increase in salt passage at acidic pH, but a slight improvement in

membrane performance at pH 10. Antony et al. (2010), who worked at pH 2-11, claimed an increase in water permeability, and in some circumstances in salt passage (when the membrane was exposed in a stirred and pressurised system) as well. Later on, Donose et al. (2013), who compared the ageing of three different RO membranes, reported the same trend as Mitrouli et al. (2010) and Kwon and Leckie (2006a, 2006b) in terms of water permeability, but concluded that salt passage results varied in a narrow interval (5%) which depended on the type of membrane. The discrepancies found in literature can be due to the different chlorination mechanisms taking place, the experimental conditions applied, such as concentration and exposure time, temperature, feed water quality, active or passive exposure, as well as the properties of the membrane assessed.

Catalytic effects of transition metal ions such as aluminium(III), copper(II) and iron(III)/iron(II) on RO membrane degradation caused by chlorine have also been reported (Gabelich et al., 2005, Kurihara and Himeshima, 1991, Tessaro et al., 2005). Tessaro et al. (2005) studied the catalytic effect of iron(III), iron(II) and aluminium(III) in RO membrane degradation processes, concluding that residual chlorine and aluminium and/or iron present in the feed RO water increased the chlorine potential oxidation in aqueous phase (the former to a greater extent) provoking negative effects on those membranes (increased salt passage and water flux).

Additionally, chlorine use in water treatment can also lead to the generation of other oxidants in presence of some anions, such as bromide and iodide. These, similarly to chlorine, can deteriorate RO membrane physico-chemical and transport properties.

In the case of bromide ions, water chlorination can lead to the formation of bromine, which has been claimed to degrade PA (Glater, 1981, Glater et al., 1985), even at very low bromide concentration (Kwon et al., 2011). The bromine formed attacks the PA by breaking hydrogen bonds between polymer chains, to a greater extent than when only chlorine is present (Kwon et al., 2011). In the case of bromine and chlorine coexistence, the former outcompetes chlorine in terms of membrane uptake and it causes a greater flux decline (Kwon et al., 2011). When chlorine is already linked to the membrane, it cannot oxidise bromide ions (i.e. bromine is not produced), not being possible its incorporation in the membrane structure (Kwon et al., 2011). The degree of degradation is also pH dependent and determining the bromine specie responsible for it is difficult because numerous and complex pH dependent reactions take place between chlorine and bromine in aqueous phase (Liu and Margerum, 2001). Other authors have attributed the degradation to hypobromous acid (Sandín et al., 2013), which can also be formed when chlorinating water in presence of bromide ions (Farkas et al., 1949), leading to bromine uptake by the membrane and breaking the polymer amide bonds (Maugin, 2013).

In the case of iodide ions, chlorine can oxidise them into hypoiodous acid (Bischel and Von Gunten, 1999) and subsequently to iodate. In the first reaction, certain anions such as borate, phosphate or carbonate have been identified as catalysers (Bischel and Von Gunten, 1999), and in the second one hydrogen carbonate and hydrogen phosphate. Also hypochlorite to hypoiodite reactions may occur in presence of iodide (Kumar and Margerum, 1987). Similarly to chlorine and bromine, hypoiodous acid can also react with membranes (Bischel and Von

Gunten, 1999), causing iodine uptake by the membrane and affecting its performance (Maugin, 2013).

Chlorine dioxide and monochloramine are used in DWTPs for disinfection and/or RO membrane biofouling control as alternatives to chlorine. Some studies have been performed aiming at elucidating their potential effects on RO membranes performance and composition.

Regarding chlorine dioxide, some discrepancies are found in literature. Sandín et al. (2013) reported chlorine increase in RO membranes after being exposed to chlorine dioxide, whereas Glater (1981), Glater et al. (1983) and Maugin (2013) did not. In terms of performance, Glater (1981) observed good resistance at neutral pH, only showing a slight increase in water flux and chloride rejection, but severe damage at pH 8.6, involving a large water flux and salt passage. Accordingly, Eriksson and Dimotsis (2012), based on experiences from various water treatment plants where chlorine dioxide was dosed, concluded that pH is a key parameter, being 8 the value above which degradation occurs. Zupanovich et al. (2012), who did not notice any salt passage raise at pH 8.4, remarked the importance of putting the membrane in service for a certain period before dosing chlorine dioxide because then the free amine sites on the membrane surface are neutralised by compounds contained in the feed water and cannot react with chlorine dioxide, decreasing the residual loss. Adams (1990) reported the water flux to be pH dependent, increasing under alkaline conditions and decreasing under acidic pH. In terms of salt passage, Adams (1990) did not notice any impact at low pH but a slight decrease at neutral or higher pH.
Besides the effect of chlorine dioxide itself on RO membranes, reagents used during its preparation, as well as compounds generated when reacting with it during water treatment may be of concern as well. For instance, during chlorine dioxide generation by-products such as chlorite, chlorate and chlorine gas may be produced, which could degrade RO membranes (Zupanovich et al., 2012). Also, chlorine dioxide is known to react with iodide, generating iodine and chlorite (Fábián and Gordon, 1997), and some authors have reported its reaction with bromide as well (Mizuta et al., 2014, Sandín et al., 2013), which could also provoke RO membrane deterioration in terms of performance and/or composition. The catalytic effect of heavy metal ions such as iron has also been suggested, enhancing the occurrence of the reaction or lowering the pH at which the degradation starts (Erikson and Dimotsis, 2012).

Concerning monochloramines, they have been claimed to chlorinate the PA active layer and to increase the permeate flux and the salt passage (Maugin, 2013), but to a lesser extent than free oxidants (Maugin, 2013, Shemer and Semiat, 2011). Some contradictory effects are reported in the literature, because other authors have noted a decrease in salt passage, attributed to an initial pore tightening (Cran et al., 2011). Within the same work, the degradation effects were associated to the formation of amidogen radicals ($NH_2^{\cdot}$), with some metals catalysing it (Cran et al., 2011, Donose et al., 2013, Gabelich et al., 2005 and 2006), which attack the PA. Some authors have hypothesized that the degradation mechanism is the same for monochloramine, chlorine and chlorine dioxide, but being monochloramine less aggressive on PA (da Silva et al., 2006, Cran et al., 2011), while others to react with the membranes differently, involving a potential addition of nitrogen (Maugin, 2013).

In presence of halogens, bromamines and iodamines can be formed, being the degree of halogen substitution on the nitrogen determined by the pH and the halogen to ammonia ratio (Shemer and Semiat, 2011). Valentino et al. (2015) experienced membrane bromination and iodination when monochloramine and bromide, and monochloramine and iodide were mixed, provoking in both cases an increase in carboxylic groups, which was attributed to the amide bond cleavage from the active layer. In terms of water and salts' passage, an increase in comparison to a pristine membrane was observed, which was consistent with the structural changes identified (increase in carboxylic groups and larger aggregate pores) (Valentino et al., 2015).

In order to avoid the harm of chlorine and other oxidants to RO membranes, sodium metabisulphite (SMBS) has often been used because of its high cost-effectiveness when dechlorinating (Fitzmann et al., 2007). Nevertheless, bisulphite effects on the RO active layer in presence of other substances naturally contained in the water to be treated or added during the treatment itself (e.g. coagulation/flocculation steps) have not been assessed before. Indeed, membrane degradation is a complex phenomenon due to the large variety of substances present in the feed water which can interfere to some extent in the degradation process. Because membrane degradation can imply premature substitution of RO membranes, with its associated costs, this work focused on the effects of a secondary oxidant, a reducing agent, a halide ion and a transition metal based catalyst not previously addressed in literature. Particularly, a methodological approach was adopted to determine the effects of chlorite, bisulphite, bromide and iron(III), alone and systematically mixed, both in terms of performance and composition, to enable water treatment utilities avoid those conditions which may lead to a decrease in membrane performance, in terms of water flux and/or solute passage. Chlorite is generated to a larger extent than chlorate and chloride in water treatment plants that use chlorine dioxide (Aieta, 1986, Odeh et al., 2002), bisulphite is commonly used upstream RO membranes to prevent their degradation by oxidising compounds, iron(III) is often used as a coagulant and hence, traces may reach the RO system and bromide is an halide ion present in some water bodies which may react with oxidants. Exposed membranes composition was characterised by RBS which provides average elements concentration on the PA active layer by penetrating 1-2 μm on membrane (PA and part of polysulfone layer) (Mi et al., 2007). Ion probing experiments provided information on structural changes of the PA. These supported the permeation results obtained, conducted with a monovalent ion (chloride) and an organic solute (rhodamine-WT), to track changes in aggregate and network pores of the PA active layer.

7.2. Materials and methods

7.2.1. Exposure experiments

RO membrane (Dow Filmtec LE 4040) exposure to potentially degrading chemicals was conducted following a protocol analogous to the one described by Valentino et al. (2015) and

Coronell et al. (2008). Chemical mixtures containing ferric chloride hexahydrate (BDH), sodium chlorite (Amresco), sodium bromide (Fisher Chemical) and sodium bisulphite (Acrós Organics) (Table 7.1) were prepared using nanopure water, sodium hydrogen carbonate (Fisher BioReagents) and sodium chloride (Sigma Aldrich), and their pH was adjusted to 6.7 by dosing sodium hydroxide and hydrochloric acid. Ambar jars were used to avoid photodecomposition. Exposure solutions were replaced daily for new fresh solutions until the target exposure time was reached (generally 9 days, otherwise specified). Previous works (Adams, 1990, Do et al., 2012b) remarked the greater halogen uptake and salt passage of those RO membranes exposed to higher concentration and short exposure time than those exposed to lower concentration and longer exposure time despite presenting the same concentration-time (mg/L·h) value. Consequently, in this work chemical concentration and exposure time were selected in such a way to allow acceleration of membrane ageing but minimising the effects of high oxidant concentration, aiming at creating conditions more similar to those from water treatment plants.

Table 7.1. Iron(III), chlorite, bromide and bisulphite based exposure solutions assessed with their corresponding concentrations.

Sample	[Fe (III)] (mg/L)	[ClO_2^-] (mg/L)	[Br^-] (mg/L)	[$NaHSO_3$] (mg/L)
I	0	0	0	0
II	1.5	0	0	0
III	0	37.5	0	0
IV	0	0	400	0
V	1.5	37.5	0	0
VI, IX, X, XI	1.5	37.5	400	0
VII	1.5	0	400	0
VIII	0	37.5	400	0
XII	0	0	0	400
XIII	1.5	0	0	400
XIV, XXII, XXIII	1.5	37.5	0	400
XV	0	37.5	0	400
XVI	1.5	37.5	400	400
XVII	0	0	0	100
XVIII	1.5	0	0	100
XIX	1.5	37.5	0	100
XX	0	37.5	0	100
XXI	1.5	37.5	400	100

7.2.2. Permeation experiments

Permeation experiments were carried out following the protocol described by Saenz de Jubera et al. (2012) using a dead-end membrane apparatus (model 8050, Millipore Co.) connected to an analytical balance (BP211S, Sartorius Co.) logged into a computer. A 400 mg/L sodium chloride (Sigma Aldrich) solution was used to assess the chloride passage, and a 5.0 mg/L rhodamine-WT (R-WT) (35% w/v aqueous solution, Turner Designs) as a surrogate for organic molecules. Chlorides were analysed by ion chromatography (Dionex IC S-2000 with a Dionex ion Pac As 18 column) and R-WT by fluorescence (excitation/emission wavelengths 550/580

nm) (RF-5301 PC, Shimadzu Scientific Instruments, Inc.) as detailed in Saenz de Jubera et al. (2012).

A modified version of the diffusion-solution model (Wijmans and Baker, 1995) which accounts for imperfections in the active layer (Urama and Mariñas, 1997) was used to fit and interpret the data. The water and solute fluxes through the membrane at steady state can be described by Eq. 7.1 and Eq. 7.2 respectively.

$$J_v = \frac{A}{(1-\alpha)} \cdot (\Delta p - \Delta \pi) \qquad \text{Eq. 7.1}$$

$$J_s = J_v \cdot C_p = B \cdot (C_w - C_p) + \alpha \cdot J_v \cdot C_w \qquad \text{Eq. 7.2}$$

The product water flux and the solute flux are represented by J_v ($m^3/(m^2 \cdot d)$) and J_s ($mol/(m^2 \cdot d)$), respectively. A ($m^3/(m^2 \cdot d \cdot MPa)$) and B (m/d) correspond to the product water and solute permeation coefficients and α is the fraction of the total product water flux corresponding to advection through membrane imperfections. $\Delta p = (p_f - p_p)$ (MPa) and $\Delta \pi = (\pi_w - \pi_p)$ (MPa) are the hydraulic and osmotic pressure differences across the membrane active layer, respectively. C (M) represents the solute concentration, and subscripts f, w, and p refer to bulk feed solution, feed solution next to the membrane wall, and permeate, respectively. The methodology used for data fitting was analogous to the described by Saenz de Jubera et al. (2012).

7.2.3. Membrane characterisation experiments (RBS)

Rutherford backscattering spectrometry (RBS) was applied to determine the composition of the membrane active layer and support, as described in Mi et al. (2007) and (2008). A 2-MeV He^+ beam generated with a Van Graaf accelerator (High Voltage Engineering Corp), whose incident, exit and scattering angles of the He^+ beam were 22.5°, 52.5° and 150°, was used, and its data was fitted using SIMNRA® software.

Besides the composition characterisation of the RO membrane, the carboxylic groups were determined by silver probing experiments ($AgNO_3$ 99%, Sigma-Aldrich), following the procedure described by Coronell et al. (2008) and (2009). Data obtained from RBS was fitted to Eq. 7.3, which describes a bimodal pore size distribution as suggested by Kim et al. (2005) and Coronell et al. (2008), to determine the associated membrane characteristics.

$$[R - COO^-] = C_{T,R-COOH} \cdot \sum_{i=1}^{n} \omega_i \cdot \frac{K_{a,i}}{[H^+] + K_{a,i}} \qquad \text{Eq. 7.3}$$

It was assumed that $[Ag^+] = [R\text{-}COO^-]$ (M), and the functional groups were at equilibrium with the ion probe solution as described in previous work (Coronell et al., 2008 and 2009). $C_{T,R-COOH}$ corresponds to the total concentration of carboxylic groups, $[H^+]$ the concentration of hydrogen ion in the ion probe solution, ω_i the fraction of functional groups with acidic constant $K_{a,i}$, and n the number of dissociation constants required to fit the data. As previously reported for other RO membranes with fully aromatic PA active layer two dissociation

constants (n = 2) resulted in the most accurate representation of the experimental data (Coronell et al., 2008 and 2009).

7.3. Results and discussion

7.3.1. Iron(III), chlorite and bromide effects

Mixtures containing iron(III), chlorite and bromide were prepared as detailed in Table 7.1 (samples I-XI) to determine the effects of each compound and their synergies when mixed on RO membranes. It is important to mention that the concentration of iron(III) was well above its solubility at the working pH, 6.7, so that significant precipitation of hydroxo-species may have occurred (Fábián and Gordon, 1991).

Elemental composition of the exposed membranes obtained by RBS analyses is listed in Table 7.2. As can be seen, trace amounts of chlorine were detected in the virgin membrane, whose presence was associated to the manufacturing process, as reported previously (Raval et al., 2010, Valentino et al., 2015). The Dow Filmtec LE4040 virgin membrane active layer elemental composition quantified corresponded to a fully aromatic polyamide, with an elemental repeating unit close to $C_{36}H_{24}N_6O_6$, as described by Coronell et al. (2008).

Table 7.2. Virgin and exposed membranes elemental composition, in atomic weight, obtained by RBS analysis.

Sample	C	H	O	N	Cl	Br	Fe
Virgin	0.4123	0.4414	0.0758	0.0696	0.0009		
I	0.4000	0.4406	0.0843	0.0740	0.0011		
II	0.4800	0.3409	0.0950	0.0783	0.0014		0.0044
III	0.4100	0.4286	0.0877	0.0710	0.0027		
IV	0.4200	0.4132	0.0900	0.0753	0.0015		
V	0.4433	0.3717	0.1013	0.0720	0.0033		0.0084
VI	0.4800	0.3208	0.1125	0.0695	0.0023	0.0016	0.0133
VII	0.4467	0.3553	0.1073	0.0780	0.0013		0.0114
VIII	0.4133	0.4254	0.0843	0.0753	0.0015	0.0002	
IX	0.4500	0.3918	0.0867	0.0683	0.0017	0.0004	0.0011
X	0.3133	0.5287	0.0850	0.0650	0.0023	0.0015	0.0042
XI	0.4333	0.3834	0.0990	0.0723	0.0013	0.0017	0.0090
XII	0.3500	0.5027	0.0760	0.0700	0.0013		
XIII	0.3533	0.4851	0.0813	0.0750	0.0011		0.0042
XIV	0.3400	0.5016	0.0787	0.0773	0.0011		0.0013
XV	0.3717	0.4813	0.0760	0.0700	0.0010		
XVI	0.3500	0.4966	0.0790	0.0700	0.0010		0.0034
XVII	0.3350	0.5281	0.0673	0.0687	0.0009		
XVIII	0.3500	0.4851	0.0807	0.0800	0.0010		0.0032
XIX	0.3300	0.5013	0.0900	0.0683	0.0051		0.0053
XX	0.3600	0.4851	0.0835	0.0670	0.0044		

XXI	0.3317	0.4842	0.0813	0.0600	0.0015	0.0372	0.0041
XXII	0.3767	0.4886	0.0667	0.0660	0.0011		0.0009
XXIII	0.3800	0.4736	0.0753	0.0673	0.0010		0.0028
XXIII + 2% citric ac.	0.3500	0.4941	0.0720	0.0820	0.0012		0.0007

The exposure to hydrogen carbonate (I sample), used as a buffer, did not result in changes in membrane composition, which confirmed its suitability to be used in exposure tests to assess RO membranes degradation. Chlorite blank sample (III sample) showed an increase in membrane chlorine content which could be attributed to a chlorination caused by this secondary oxidant. The rest of the samples exposed to chlorite but VIII sample (which contained chlorite and bromide) also suffered an increase in chlorine content in terms of active layer composition. In acidic pH chlorite disproportionates and produces chlorine dioxide (Gordon et al., 1972) which, according to some authors, can encompass an increase in chlorine content in RO active layer (Mizuta, 2014, Sandín et al., 2013), which could explain the results obtained; although other authors have claimed no chlorine increase in PA after chlorine dioxide exposure (Glater et al., 1983, Maugin 2013). However, at the working pH, 6.7, chlorite solutions are reasonably stable when kept away from light and heat, and their products are chlorate and chloride rather than chlorine dioxide according to Gordon et al. (1972). Consequently, it may be deduced that chlorite itself caused the membrane chlorination. In the case of VIII sample, as described later on, chlorite could have been consumed by reacting with bromide ions (Simoyi et al., 1985) hence not leading to an increase in chlorine content in the membrane.

Iron(III) blank sample (II sample), similarly to all samples exposed to iron(III), presented iron in its membrane composition and an increase in oxygen content. An increase in oxygen content could be caused by the carboxylic groups formed by the breakage of the amide bond from the PA active layer. Nevertheless, after cleaning the membranes with 2% w/w citric acid (Fischer Chemical) both concentrations decreased to levels similar to those of the virgin membrane (data not shown). As a result, these changes in oxygen content may be attributed to the presence of iron oxides' precipitates, which would be expectable taking into account that the solubility limits were surpassed, rather than a cleavage of the amide bond.

Bromide exposure (IV sample: bromide blank) did not cause any effect on membrane composition, confirming that the reduced form (bromide ion) cannot bind to the RO membrane. This also happened in the case of bromide and iron(III) exposure (VII sample), where complexes may be formed (e.g. $FeBr_3$ (Gregory and Laughlin, 1977)), but bromide may not change its oxidation state (-1). However, in presence of an oxidant (VIII sample), an uptake of bromine occurred; in this case 0.016% in atomic weight. A potential explanation of the bromine uptake by the membrane in presence of bromide and chlorite would be the oxidation of the former leading to bromine, as described by Simoyi (1985). Bromine is expected to oxidise amides, slowly, (Heeb et al., 2014), and thus, could explain the uptake by the membrane, as reported by other authors (Glater, 1981, Glater and Zachariah, 1985, Kwon et al., 2011). Nevertheless, it is important to mention that the study of Simoy (1985) was performed at much lower pH (0.4 – 2.5) so that his results cannot be directly applied.

In presence of iron(III), together with chlorite and bromide, the incorporation of bromine in the active layer (sample VI) was about 10 fold higher (accounting for 0.16% in atomic weight) than without iron(III) (sample VIII). The greater bromine uptake in presence of iron(III) could be explained by the catalytic effect of the latter on the disproportionation of chlorite: the complex $FeClO_2^{2+}$ is formed, which decomposes into chlorine dioxide and iron(II) (Fábián and Gordon, 1991, Fábián and Gordon, 1992, Fábián, 2000). Chlorine dioxide could react with the bromide ions present and generate hypobromous acid (Mizuta, 2014, Sandín et al., 2013), which is known to be uptaken by the membrane (Glater et al. 1983, Sandín et al., 2013), and degrade its performance (Glater et al., 1983, Sandín et al., 2013). Among the various reactions involved in the mechanism of chlorite disproportionation to chlorine dioxide described by Fábián and Gordon (1992), hypochlorous acid is also formed, which is known to react with bromide (Deborde and von Guten, 2008, Heeb et al., 2014) and thus, could also explain the uptake of bromine experienced. The fast catalytic decomposition of the complex $FeClO_2^{2+}$ would lead to a greater chlorine dioxide and hypochlororous acid concentration which in turn would produce more hypobromous acid and ultimately incorporate in the RO membrane, as chlorine and/or bromine. Bromine is usually more reactive than chlorine (Deborde and von Guten, 2008) and it has been stated to damage the PA to a larger extent than chlorine (Shemer and Semiat, 2011). Additionally, according to Kwon et al. (2011) bromine uptake is more favoured than chlorine uptake, which is in agreement with VI sample composition. Fábián and Gordon (1991), Fábián and Gordon (1992) and Fábián (2000) works on $FeClO_2^{2+}$ formation and decomposition were conducted under acidic pH. Nevertheless, Gordon (1989) noted that trace amounts of Fe(III) could reduce half-life of chlorite oxidation by chlorine and/or hypochlorous acid reactions from many hours/days to few seconds at neutral pH. A similar effect of iron(III) could take place so that the formation of the complex $FeClO_2^{2+}$ and its subsequent decomposition into chlorine dioxide could occur under the experimental conditions of this work, despite not being acidic.

In case the bromine formation reported by Simoyi (1985) would take place, no catalytic effects of iron(III) are reported in the literature. Nevertheless, both mechanisms could occur, being one or the other more favoured according to the experimental conditions (e.g. presence/absence of iron(III)). Hypothesis of the compounds and/or reactions that may occur are made, but the identification of the compounds formed under each circumstance is beyond the scope of this work, especially taking into account the complexity of the chlorine and bromine chemistry. Apart from the products that may be formed, these can further react, increasing the difficulty of their identification. For instance, if hypochlorous acid is formed, besides reacting with bromide to generate hypobromous acid (Deborde and von Guten, 2008, Heeb et al., 2014), it could also react with chlorite to generate chlorine dioxide (Tang and Gordon, 1984). Hypobromous acid has also been claimed to react with chlorite to generate chlorine dioxide through BrCl, a highly reactive specie (Odeh et al., 2004), to disproportionate into bromide and bromate, through BrO_2^- (Heeb et el., 2014) and to form bromine which can react further to Br_3^- and bromate, despite being a slow process at pH 6-8 (Heeb et al., 2014).

Membrane performance in terms of chloride passage of samples I-XI is shown in Figure 7.2 and permeation parameters (water and chloride from Eq. 7.1 and Eq. 7.2) summarised in Figure 7.3. The membranes which experienced an increase in chlorine concentration in their active layers (Table 7.2) presented a raise in their water permeation coefficient (A) (Figure 7.3 black

bars). In particular, the sample exposed to chlorite and iron(III) (V sample) showed a 1.43 fold increase, the one to chlorite, iron(III) and bromide (VI sample) 1.21, and the chlorite blank (III sample) 1.13 compared to the virgin membrane water permeation coefficient (A_0). Maugin (2013) also experienced a simultaneous increase in chlorine content and in water permeability in his case when RO membranes were exposed to hypochlorous acid. The rest of the samples assessed did not show significant increases from a water permeability perspective compared to the virgin membrane.

Regarding chloride passage, the exposure condition that led to a greater chloride passage was the one with iron(III) (II sample, B/B_0 2.90), followed by iron(III), chlorite and bromide (VI sample, B/B_0 1.75) and finally, iron(III) and bromide containing solution (VII sample, B/B_0 1.25) (Figure 7.3, grey bars). In the case of iron(III), chlorite and bromide, as discussed before, may be due to hypobromous acid formation, which is known to cause a raise in chloride passage (Maugin, 2013), and would be in accordance with the increase in bromine quantified in the active layer of the membrane (Table 7.2). In addition to this, the fact that all the conditions that caused a certain increase in chloride passage were those where iron(III) was dosed may suggest that (hydrated) iron particles may incorporate in the network pores, enlarging them and thus enabling a greater monovalent ions passage. Nevertheless, the sample where chlorite and iron(III) was dosed (V sample) did not show this behaviour and hence, it is difficult to hypothesize an increase of network pores size by iron particles. Some studies also reported an increase in salt passage by RO membranes exposed to ferric chloride coagulant residuals, but attributed the degradation to a catalysing effect of residual iron(III) to a chlorine-amide reaction on the membrane surface, despite having quenched chlorine (Gabelich et al., 2002). Kavitskaya et al. (2000) also experienced an irreversible increase in sodium passage when filtering calcium sulphate solutions in presence of iron(III), which attributed to the formation of a deposit of colloids and flocs of iron(III). Nevertheless, cleaning strategies to assess whereas rejection could be recovered (and hence determine if fouling was the cause) were not undertaken. Therefore, iron(III) could also be responsible for the results reported in that study.

The rest of the samples assessed did not show significant differences in the chloride permeability coefficient (B) than the virgin membrane (Figure 7.3). Therefore, their network pores, responsible for the chloride rejection, were not affected in these cases.

In terms of R-WT passage (data not shown), no significant changes were experienced in any of the samples, suggesting that aggregate pores, which are the ones that R-WT can diffuse through because of its size (0.88 nm in diameter (Saenz de Jubera et al., 2012)), were not affected.

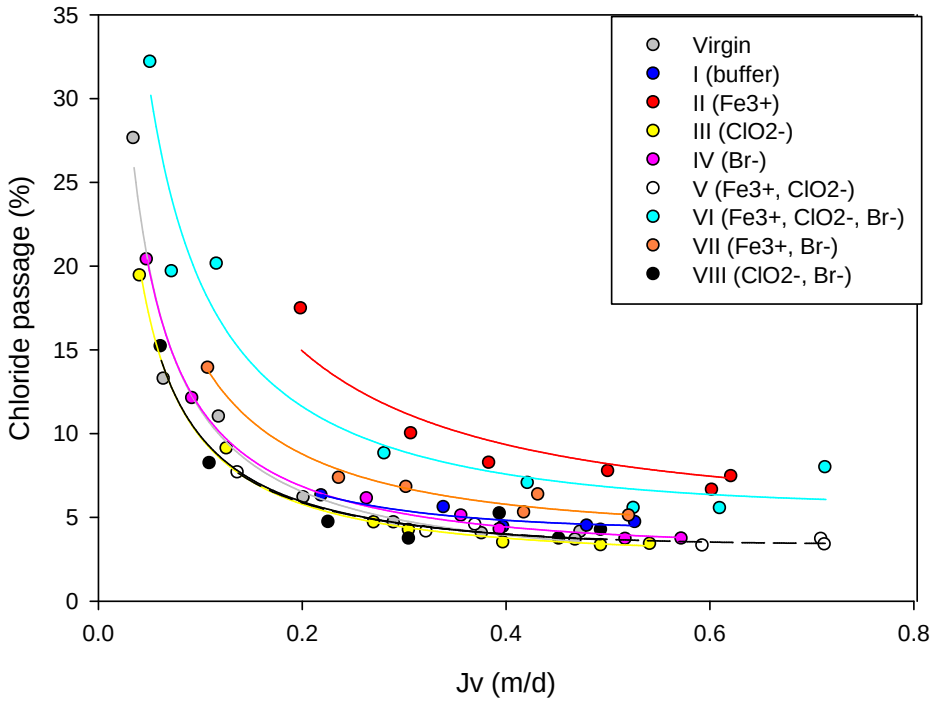

Figure 7.2. Chloride passage as a function of water flux for membranes I, II, III, IV,V, VI, VII and VIII (dots: experimental data; lines: fitted values). Solute permeation parameters are plotted in Figure 7.3.

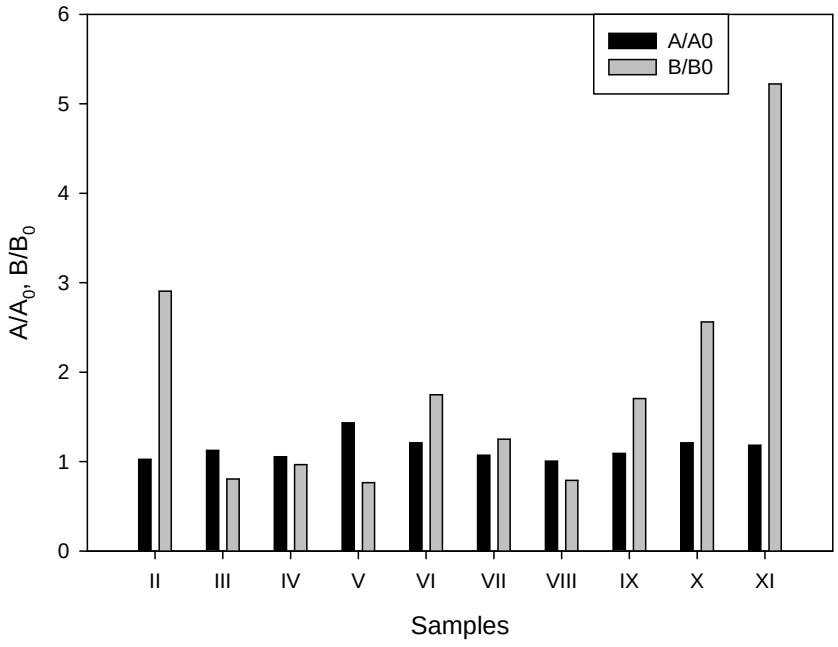

Figure 7.3. Relative permeation coefficients of water (A/A_0, black bars) and chloride (B/B_0 grey bars) of the samples II, III, IV, V, VI,VII, VIII, IX, X and XI (comparison with the virgin membrane values A_0, B_0).

Under the condition causing greater bromine uptake (VI sample), a kinetic study was performed. Samples with 4 (IX sample), 9 (VI sample), 18 (X sample) and 55 (XI sample) days exposure were assessed and results are shown in Figure 7.4. It can clearly be seen that the greater the exposure, the higher the membrane degradation in terms of chloride passage. A relative chloride permeation coefficient of 5.2 (B/B_0) was reached after 55 days exposure (XI sample), involving a salt passage of 14% approximately. Regarding bromine incorporation in the active layer of the membrane (Table 7.2), a fast initial increase was followed by a slower rate afterwards, which is in accordance with Maugin (2013) experiments conducted with bromine based compounds. After 55 days of exposure, bromine accounted for 0.17% of the active layer composition. In terms of water permeability, there was an initial increase and afterwards apparently the water permeation coefficient reached a plateau, at A/A_0 1.2 approximately. No differences were found in R-WT permeation tests among the different samples assessed (data not shown). Based on these results it could be suggested that membrane bromination occurred in a relatively fast period when water permeability was also affected, but its main effect, on chloride passage, was a progressive time dependent process.

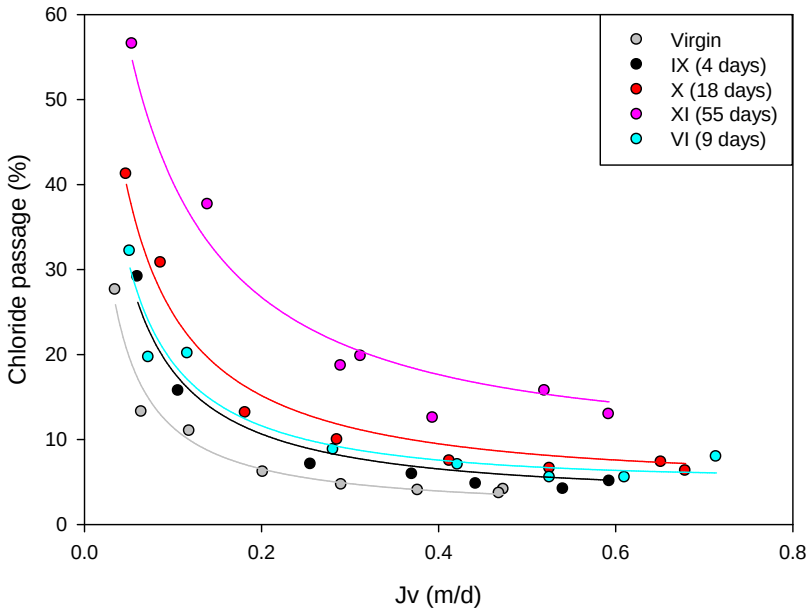

Figure 7.4. Chloride passage as a function of water flux for membranes XI, VI, X and XI (dots: experimental data; lines: fitted values). Permeation parameters are plotted in Figure 7.3.

7.3.2. Bisulphite, iron(III), chlorite and bromide effects

Two main sets of experiments were carried out to elucidate bisulphite effects on RO membranes composition and performance: one set of samples contained a greater bisulphite molar concentration than the stoichiometrically needed to reduce the chlorite dosed (2:1 according to Gordon et al., 1990), which was the same concentration as in the previous experiments (37.5 mg/L) (samples XII - XVI), and the second set of samples with a lower concentration than the stoichiometrically required (samples XVII – XXI).

The membranes exposed to an excess of bisulphite relative to chlorite (samples XII, XIII, XIV, XV, XVI from Table 7.1) did not present major dissimilarities in terms of composition (Table 7.2): only those samples exposed to iron(III) were different to the virgin membrane. Analogously to the previous experiments, iron was incorporated to the active layer, but lower amounts were encountered: 0.1 – 0.4% in atomic weight (before 0.4 - 1.4). Because bisulphite was in excess compared to chlorite, a reducing environment was created, not enabling the bromide ion to be oxidised and hence, to incorporate in the membrane active layer (XVI sample), as happened when bisulphite was not dosed (VI sample). In addition to this, because of the reducing environment, no chlorine content increase in the membrane was experienced among those samples exposed to chlorite (XIV, XV, XVI). From a water permeability perspective, no changes were found, as shown in Figure 7.3 and Figure 7.5 (black bars), with most of the samples presenting a similar water permeability coefficient as the virgin membrane (A_0).

Nevertheless, chloride passage was severely affected (Figure 7.3 and Figure 7.5 grey bars, Figure 7.6). Nine days of 400 mg/L sodium bisulphite exposure (XII sample) resulted in doubling the chloride permeation coefficient, leading to a chloride passage of 6% approximately (B/B_0 2.4). In the case of chlorite and bisulphite dosage, because bisulphite was in excess compared to chlorite, after reducing the chlorite some may be left, leading to an increased chloride passage (XV sample) compared to a virgin membrane (B/B_0 1.6), but to a lesser extent than the bisulphite blank sample (XII sample). When dosing iron(III) in presence of bisulphite at the working pH, a dramatic raise in chloride passage was experienced (XIII, XIV samples), achieving values of 15 - 12%, which corresponded to solute permeation coefficients 4.5 – 5.5 fold the virgin membrane one. In the case of bisulphite, chlorite, iron(III) and bromide (XVI sample) the chloride permeation coefficient relative to the virgin membrane one (B/B_0) was 2.6.

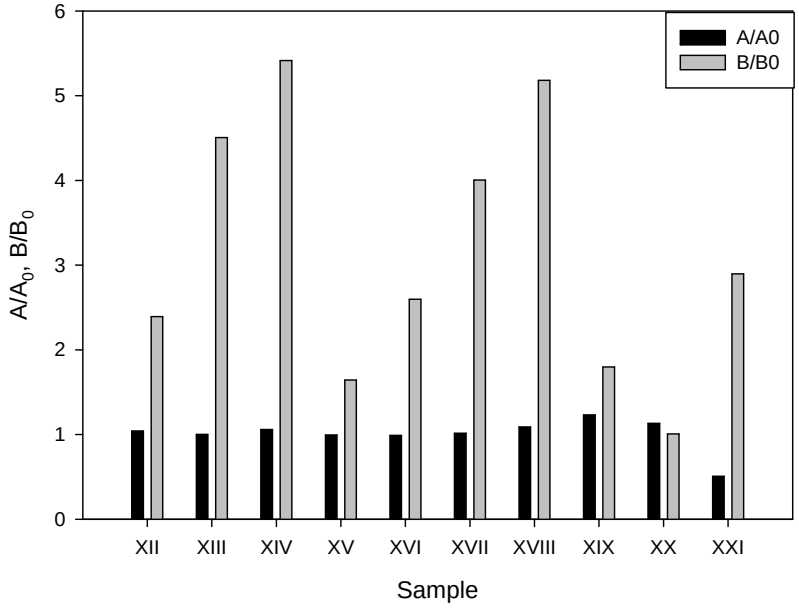

Figure 7.5. Relative water (A/A_0 black bars) and chloride (B/B_0 grey bars) permeation coefficients of the samples XII, XIII, XIV, XV, XVI,XVII, XVIII, XIX, XX,XXI compared to the virgin membrane ones.

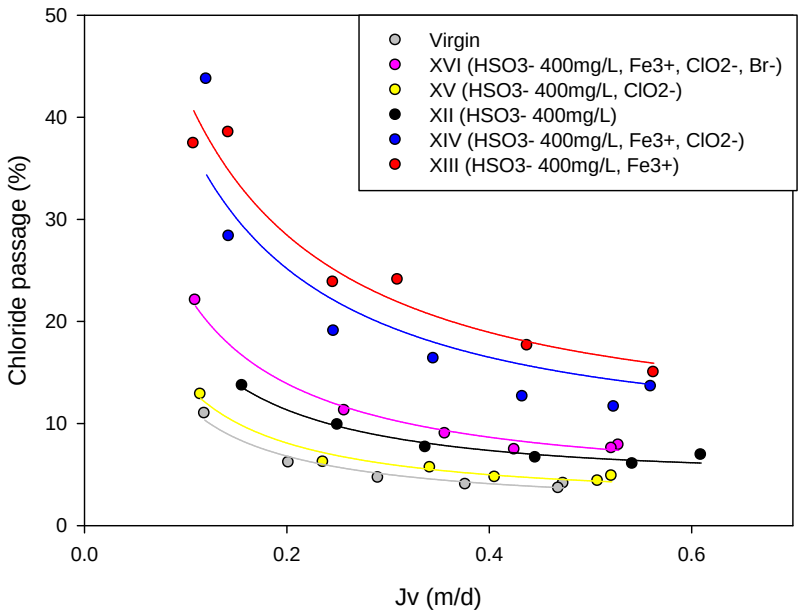

Figure 7.6. Chloride passage as a function of water flux for membranes XII, XIII,XIV, XV and XVI (dots: experimental data; lines: fitted values). Permeation parameters are plotted in Figure 7.3.

A second set of samples with bisulphite concentration lower than the stoichiometrically required to reduce chlorite was studied (XVII, XVIII, XIX, XX, XXI samples from Table 7.1). In this case, there were some differences in terms of composition in comparison with the virgin membrane, particularly those exposed to iron(III) (XVIII, XIX, XXI samples), to bromide (XXI sample) and to chlorite (XIX, XX samples) together with bisulphite, as shown in Table 7.2. In the case of membranes exposed to iron containing solutions, iron incorporation occurred, presenting similar values to the previous set of samples: 0.3 – 0.5 % in atomic weight. Those membranes soaked in chlorite and bisulphite (XIX, XX samples) presented an increased concentration in chlorine in the active layer compared to the virgin membrane, possibly indicating a chlorination event, as experienced before. In the case of the bromide containing solution (XXI sample: bromide, bisulphite, chlorite and iron(III)) large amounts of bromine were uptaken by the membrane, achieving 3.7% of the atomic weight of the active layer. Because chlorite was in excess compared to bisulphite, bromide ion could be oxidised and hence, be incorporated in the membrane. Nevertheless, taking into account that in the initial experiments, where the maximum bromine uptake was 0.16% of atomic weight (VI sample), a different mechanism may be involved to explain this almost 25 fold difference.

In terms of water permeability, most of the membranes performed like the virgin membrane, except the one exposed to bromide, bisulphite, chlorite and iron(III) (XXI sample) whose water permeability coefficient dropped to half approximately (A/A_0 0.51); the one soaked into bisulphite, chlorite and iron(III) (XIX sample), which increased by 1.23 fold; and the one exposed to chlorite and bisulphite (XX sample), by 1.13 (Figure 7.3 and Figure 7.5 black bars). Again, those samples presenting greater water permeability were those which showed an increased chlorine content, reinforcing the hypothesis of a chlorination event caused by chlorite exposure. Concerning R-WT passage, no major differences were noticed in any case (data not shown).

Chloride passage assessment of this set of samples (Figure 7.5 grey bars and Figure 7.7) also indicated the degradation caused by bisulphite (4.0 fold increase in terms of chloride permeation coefficient and values of 10.0% in chloride passage; XVIII sample) and the synergistic effect in presence of iron(III) (XVIII, XIX samples) under the conditions assessed. When comparing these last two samples, XVIII presented a 5.2 fold increase in chloride permeation coefficient whereas XIX, 1.8. This could be attributed to the presence of chlorite in the later scenario, which would consume bisulphite (limited) and hence, damage the membrane to a lesser extent. In the equivalent conditions of the previous set of data (XIV sample), where bisulphite was in excess, chloride permeation coefficient increase was 5.4 fold the virgin membrane one, which would support this hypothesis.

XX sample reinforced the synergistic effects of iron(III) and bisulphite, since the chloride permeation coefficient was virtually the same as the virgin membrane (Figure 7.3) when iron(III) was not dosed. Bromide, chlorite, iron(III) and bisulphite (XXI sample) also turned out into a 2.9 fold increase in chloride permeation coefficient (Figure 7.5).

Previous works claimed the generation of oxidising agents when sodium bisulphite was dosed in presence of heavy metal ions, chloride ion and dissolved oxygen in a neutral pH solution (Nagai et al., 1994). Particularly, several authors (Ziajka et al., 1994; Reddy and van Eldik 1992, Brandt et al., 1994) described an autooxidation process of bisulphite catalysed by iron(III) where free radicals are generated. 1:1, 1:2 and 1:3 sulfito complexes can be formed, depending on the total S(IV) concentration used (Kraft and van Eldik, 1989a), being SO_4^{2-} and $S_2O_6^{-}$ the main oxidation products (Kraft and van Eldik, 1989b). The transition metal-sulfito complexes decompose spontaneously and the sulphite radical, $SO_3^{\bullet-}$, and the reduced form of the metal are produced (Brandt et al., 1994). In absence of oxygen, SO_4^{2-} and $S_2O_6^{2-}$ are generated; when oxygen is present, peroxomonosulphate radical, $SO_5^{\bullet-}$, a strong oxidant, is also formed, which can react with HSO_3^{-} or Fe(II) to produce HSO_5^{-} (Brandt et al., 1994). Greater Fe(III) and S(IV) concentrations result in a higher formation rate of $SO_3^{\bullet-}$ (Brand et al., 1994). The ratio of Fe(III), Fe(II) and S(IV) versus oxygen is important in the overall decay of the iron(III)-sulphite complexes (Brandt et al., 1994), varying the oxidation pathway with the ratio bisulphite/iron (Ziajka et al., 1994).

The reactivity of bisulphite with bromine-based species has been reported in literature (Khan et al. 2003) and the autocatalytic nature of bisulphite with bromine based species too (Wang et al. 2012). Li et al. (2015) investigated the formation of bromate when Co(II) reacted with peroxymonosulphate by means of the sulphate radical, $SO_4^{\bullet-}$, with $Br^{\bullet}$ and $Br_2^{\bullet}$ as intermediates. It was noted that $SO_4^{\bullet-}$ could oxidise Br^{-} to $Br^{\bullet}$, generating bromine, hypobromous acid, OBr^{-} and ultimately bromate. Similar reactions involving the formation of bromine active species could be envisaged, which could explain the large amount of bromine uptaken by the membrane when bisulphite, iron(III), bromide and bisulphite in excess were studied (XXI sample).

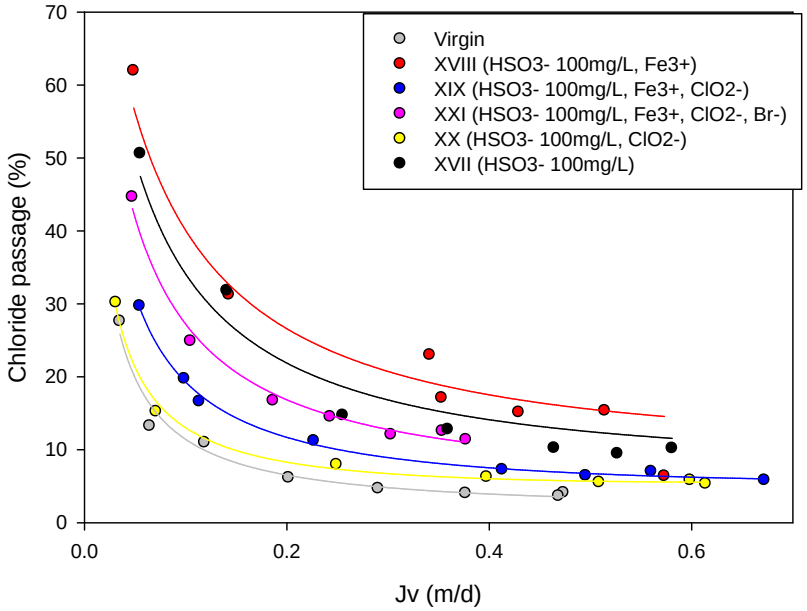

Figure 7.7. Chloride passage as a function of water flux for membranes XII, XIII, XIX, XX and XI (dots: experimental data; lines: fitted values). Permeation parameters are plotted in Figure 7.3.

Both sets of data provided consistent results. Considering chloride passage effects, it could be concluded that in presence of bisulphite alone, degradation occurred in the conditions tested (XII, XVII samples). When combined with iron(III) (XIII, XVIII samples), chloride permeation coefficient increased 4.5 – 5.2 fold (B/B_0) compared to a virgin membrane, achieving values of 15% of chloride passage. When dosing chlorite below the stoichiometrically required dose compared to bisulphite and in presence of iron(III) (XIV sample), significant degradation occurred (B/B_0 5.4); whereas in excess (XIX sample) the effects were more limited (B/B_0 1.8). This may be due to the oxidation of bisulphite by chlorite, hence limiting the bisulphite capable of reacting with iron and thus, the membrane degradation extent. Nevertheless, still some degradation took place because as shown previously, chlorite effect (III sample) was much lower. Therefore, the kinetics of the mechanism where free radicals are generated may be the same order of magnitude than the redox reaction between bisulphite and chlorite and thus, some degradation is still carried out. When bisulphite and chlorite were present (XV, XX samples), but without iron(III) dosage, the effect depended on the stoichiometric amount dosed: when bisulphite was limiting, no significant degradation in terms of chloride passage was suffered. But there was certain chlorination and a slight increase in water flux. The effect cannot be totally attributed to chlorite because its blank (III sample) presented a decrease in chloride passage and XX sample did not. When bisulphite was in excess, there was a certain increase in chloride passage (B/B_0 1.6), but to a lower extent than bisulphite alone. In this case, chlorination and increased water passage were not experienced. Both in excess and defect of bisulphite, when iron(III) was not dosed, the extent of the impact on chloride passage was much lower than when present, evidencing its catalytic effect.

Taking into account that when chlorite was in excess compared to bisulphite (XX sample) the membrane performance was not like the chlorite blank (III sample), or that when bisulphite was in excess compared to chlorite (XV sample) the effect was not as pronounced as with

bisulphite alone; or when iron(III), bisulphite, bromide and chlorite in excess did not behave like the analogous sample without bisulphite (VI sample) it can be hypothesized that fast reactions with intermediates play a role within this chemistry.

The free radicals generated in the bisulphite autooxidation catalysed by iron(III) species could be the responsible for the increase in chloride passage experienced. Because of the free radical nature, the process could be sensitive to time (i.e. from bisulphite mixing point to membranes location), so that full scale plants may have not been affected by this process. In addition to this, due to their radical nature, membrane autopsies would not probably enable the identification of the origin of the degradation. Martin and Li (1996) concluded that the kinetics of the catalysis of bisulphite oxidation by aqueous iron(III) strongly depended on pH and ionic strength, and that the reaction mechanism was very complex in itself. In addition to this, in natural water, radicals, intermediates and heavy metal ions could react with natural organic matter (NOM), $SO_4^{\bullet-}$ radicals could be scavenged by some anions like hydrogen carbonate and carbonate (Li et al., 2015), or some species could react with oxygen, not leading to the detrimental effects on RO membranes observed in this work. Sommariva et al. (2012) reported the same phenomena in a seawater RO plant where sodium bisulphite was overdosed in presence of heavy metal ions. The plant suffered an increased salt passage and no halogens were detected in the membrane surface. The dosage of a chelating agent, EDTA, which complexed with iron(III), prevented the membrane degradation to occur, evidencing the catalysing effectof the heavy metal ions. Also, unintentionally, Gabelich et al. (2002) experienced a significant increase in salt passage in RO membranes when bisulphite was dosed to water pre-treated with $FeCl_3$ (4.0 - 5.0 mg/L). Gabelich et al. (2002) attributed this decay in performance to residual iron(III) catalysing a chlorine-amide reaction on the membrane surface (despite having quenched residual chlorine and obtaining negative results on free chlorine residuals in feed water); nevertheless, based on the results obtained in this work, it could be attributed to the bisulphite and iron(III) synergistic effects.

It is important to mention that the reported mechanisms of the catalysed autooxidation of bisulphite involve the existence of iron(II) besides iron(III). Gabelich et al. (2005) and Cran et al. (2011) described the catalysing effect of iron(II) on monochloramines effect on PA degradation. Therefore, the effect of iron(II) cannot be discarded in the considered system and should be further investigated.

Under the condition causing greater chloride passage (sample XIV, containing iron(III), chlorite and bisulphite in excess) a kinetic study was performed. Membranes exposed to such mixture for 4 days (XXII sample) and 23 days (XXIII sample) were characterised in terms of composition and performance. Similarly to the previous results, the only difference compared to the virgin membrane composition was the incorporation of iron, being higher at longer exposure times (Table 7.2). In terms of water and R-WT permeation coefficients (data not shown) and chloride passage (Figure 7.8) no significant differences were found among the samples, suggesting that the degradation (only experienced in terms of chloride passage) was a fast process, causing a severe effect at low exposure times and not significantly increasing afterwards.

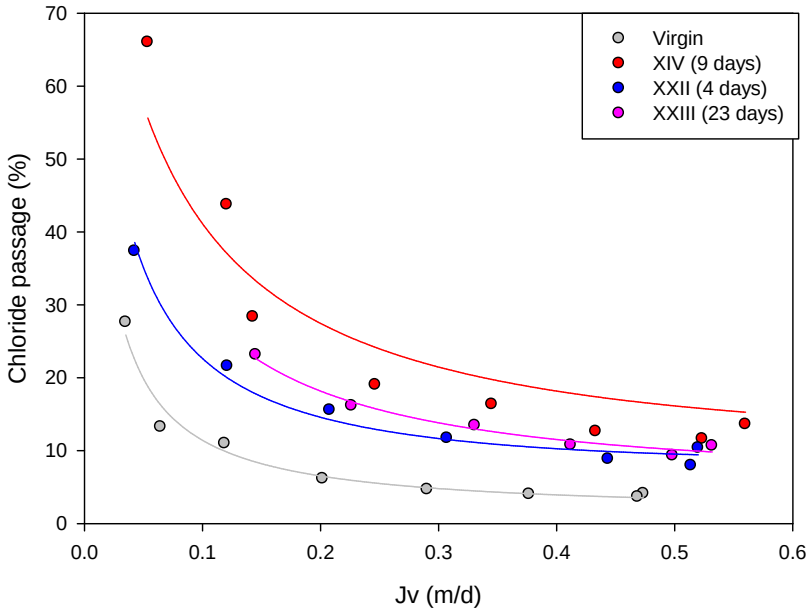

Figure 7.8. Chloride passage as a function of water flux for membranes XIV, XXII, and XXIII (dots: experimental data; lines: fitted values). Permeation parameters are plotted in Figure 7.3.

Aiming at determining structural changes in the bisulphite, iron(III) and chlorite degraded membrane (XXIII sample), silver probing experiments, to titrate the accessible deprotonated carboxylic groups from both the virgin and the exposed RO membrane were carried out following Coronell et al. (2008) procedure (pH: 4.5 – 10.5). The RBS characterisation of the virgin membrane used (Dow Filmtec LE4040) has not been published before, neither in terms of chemical composition nor in pores size distribution. Compared to other reported RO membranes, LE4040 carboxylic content was lower (0.31 M versus 0.50 – 0.64 M) (Figure 7.9), which is consistent with the slightly lower carbon and oxygen content quantified in its active layer (Table 7.2) (Coronell et al., 2010).

Silver probing experiments (Figure 7.9) showed that the total number of carboxylic groups did not differ between the virgin membrane and the membrane exposed to bisulphite, iron(III) and bisulphite (XXIII sample) (0.31 M vs. 0.28 M), which is in accordance with the constant concentration of oxygen reported from the samples analysed. This means that the exposure conditions did not cause amide bond cleavage, which would have led to more carboxylic and amine groups. However, an increase in the fraction of aggregate pores (associated to the acid-base equilibrium pKa_1) could be appreciated, since ω_1 from Eq. 7.3 increased, particularly from 0.28 of the virgin membrane to 0.41 of the exposed membrane (XXIII sample) (Figure 7.9). Also, the decrease of pKa_2 (from 8.73 to 8.20) indicated that network pores increased in size. The two phenomena explain the increase in the chloride passage quantified in the permeation experiments. The lack of changes in pKa_1, corresponding to the size of aggregate pores, is in agreement with no changes on the R-WT passage experienced.

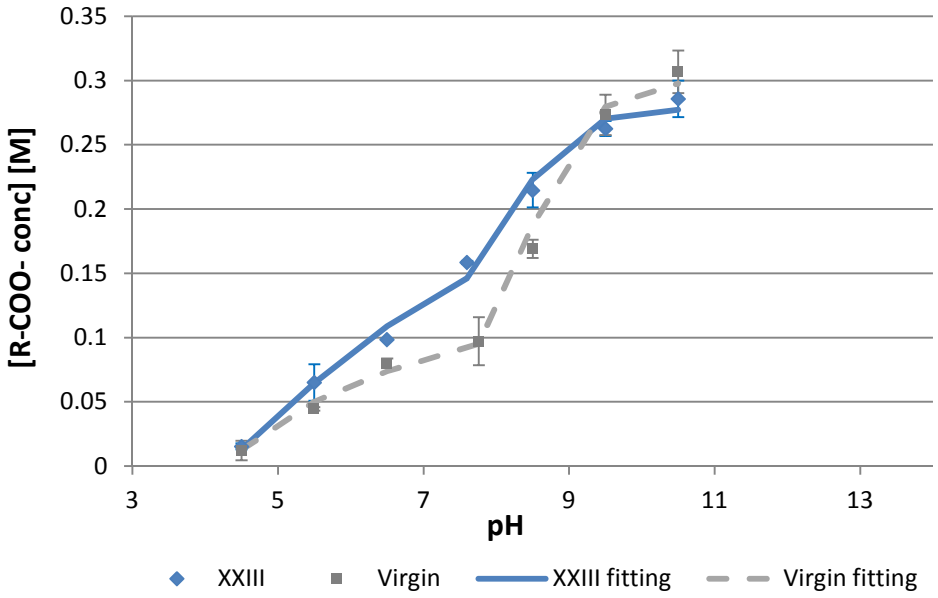

Figure 7.9. Titration curve from a virgin membrane (grey, dotted) and a membrane exposed to bisulphite, iron(III) and chlorite (blue, continuous) (sample XXIII). Dots correspond to experimental values and lines to the fitted ones (Eq. 7.3).

7.4. Conclusions

Different effects were observed when exposing RO membranes to mixtures based on iron(III), chlorite, bromide and bisulphite in terms of membrane performance (water and chloride passage mainly), composition and morphology. Based on the results obtained, it can be concluded that under the condition tested, iron was incorporated to the membrane, and probably it was deforming the network pores, leading to an increase in chloride passage. Nevertheless, water and R-WT passage was not affected. When iron and bromide were mixed, a similar effect was suffered but to a lesser extent. It is supposed that iron-bromide complexes were formed, so that less iron was available to interact with the membrane. Because bromide oxidation state was not modified, it did not interact with the membrane. In the case of chlorite exposure, a secondary oxidant formed when dioxichlorinating water for instance, it involved an increase in chlorine content in the RO membrane active layer and under the conditions addressed, provoked an increase in water permeability (A/A_0 1.13) and a decrease in chloride passage (B/B_0 0.81). These symptoms have been described by several authors as the initial stages of membrane chlorination, which afterwards result in a dramatic increase of chloride passage and water flux (Kang et al., 2007, Glater, 1981). Taking into account the chlorite stability at nearly neutral pH reported (Heeb et al., 2014), it could be hypothesized that the chlorite itself led to the chlorination of the active layer of the RO membrane and affected its performance, showing a similar behaviour to hypochlorous acid, but to a lesser extent.

Under the conditions tested, when chlorite and iron were blended, the effects of chlorite prevailed: water flux raised and chloride passage decreased. In terms of composition, the membrane chlorine content slightly increased, and iron was incorporated as well.

In the case of bisulphite exposure an increase in chloride passage was experienced (6.0 – 10.0%), but no changes in the membrane composition were identified. The effect of chlorite and bisulphite blended depended on their relative proportion, being more pronounced those effects associated to the compound with greater stoichiometric molar concentration (1:2 according to Gordon et al., 1990).

The mixture of bisulphite and iron(III) resulted in a severe increase in chloride passage, achieving values up to 15.0% after 9 days exposure. It is hypothesized that an autooxidation of bisulphite catalysed by iron(III) occurred, generating highly reactive species which interacted with the membrane, negatively affecting its performance (increased chloride passage). Because of the radical nature of these species, no changes in membrane composition were observed. When dosing bisulphite, iron(III) and chlorite, there was always an increase in chloride passage (6.0 – 12.1%), but the extent varied according to the bisulphite and chlorite molar ratios; water flux could be affected or not based on the relative concentrations as well. The process was fast, affecting the membrane during the initial exposure and not increasing significantly afterwards. It was shown by silver probing experiments analysed by RBS that the amide bonds from the PA active layer were not broken, but the size of the network pores increased (pka_2 = 8.2 vs. 8.7 from the virgin membrane). In addition to this, the proportion of network pores diminished (0.59 vs. 0.72 from the virgin membrane), hence, the fraction of aggregate pores raised (from 0.28 of the virgin membrane to 0.41 from the exposed membrane). These two effects explain the increase in chloride passage experienced. The size of the aggregate pores was not modified (pka_1 did not differ), which is in accordance with the lack of affection in terms of R-WT passage.

When bisulphite, iron(III), chlorite and bromide were mixed the effects differed, again depending on the relative quantity of bisulphite and chlorite. In both cases the chloride passage increased to a similar extent (8.5 – 11.3%), but in excess of chlorite significant bromination of the membrane took place. No increase in chlorine content was noticed in the RO active layer, which would be in accordance with the greater affinity for bromine than chlorine reported (Kwon et al., 2011). It is thought that free radicals generated when bisulphite was limiting oxidised bromide to $Br^{\cdot}$ or $Br_2^{\cdot}$, which interacted with the membrane and led to its uptake by the PA. Besides the bromination, a large decrease in water passage was shown, which could be due to the collapse of the polymer chains caused by the high bromine uptake, breaking the PA membrane bonds (Maugin, 2013) or the hydrogen bonds (Kwon et al., 2011). When bisulphite was in excess, because of the reducing environment generated, no bromine and chlorine were uptaken by the PA. Also, under these conditions water permeability coefficient did not differ from the virgin membrane one.

Bromide itself was not uptaken by the membrane, but when combined with chlorite, an oxidant, a small incorporation was noticed. Several hypotheses can be drawn, among them the oxidation of bromide to bromine by chlorite (Simoyi, 1985). Bromine could be transformed into other species, such as hypobromous acid, and this to others, like Br_3^- or bromate. Consequently, due to the complexity of the chlorine and bromine chemistry, it is difficult to determine which species led to the bromine membrane content increase in the PA active layer. In terms of performance, the chloride passage slightly decreased (chloride passage accounted

for 3.9%) and the water flux was not modified. Because the bromine uptake by the membrane was minor, probably the effects in terms of membrane performance were not noticeable under the tested conditions. On the other hand, when mixing bromide, chlorite and iron(III), a 10 fold increase in bromine uptake by the membrane was observed. This is probably due to the catalytic effect of the iron(III) to the chlorite disproportionation (to chlorine dioxide through the complex $FeClO_2^{2+}$ and generating hypochlorous acid within the mechanism), causing a greater amount of hypobromous acid, which ultimately turned into the incorporation of bromine in the membrane. In this case, a certain chlorination occurred, but to a lower extent than bromination. The chloride passage increased, and it showed to be a progressive process, with greater degradation after longer exposure time, achieving values up to 14.3% of chloride passage after 55 days exposure. Water flux was slightly raised (1.18 fold the virgin membrane one) and apparently reached a plateau after the initial increase. Hypobromous acid effects on RO membrane have been reported to be similar to the experienced ones under these conditions.
Further studies to determine the reactions and compounds involved in the degrading mechanisms identified within this study should be explored to better understand and control them.

Taking into account the results obtained, water treatment facilities should carefully control iron(III) dosage upstream RO membranes in order to minimise its effects, due to the increased chloride passage it can provoke, as well as the catalytic effects it presents, in this case with bisulphite and with chlorite and bromide, which also cause a raise in chloride passage. Particularly, the increase in chloride passage provoked by bisulphite and iron(III) under the tested conditions, may lead to a chloride passage well above the process specifications, requiring premature replacement of the RO membranes. From a structural standpoint, this exposure causes a raise in the fraction of aggregate pores and in the size of network pores, but does not involve PA bond cleavage. Finally, the bisulphite dosage required upstream RO membranes should be determined in each case in order to avoid over dosing which could lead to undesired membrane performance as well.

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CHAPTER 8

Conclusions and Outlook

8.1. Conclusions

Although some previous studies demonstrated the feasibility of direct UF, the scale of the experiments, their duration or the characteristics of the feed water required further testing. This thesis demonstrated the technical, sanitary and operational feasibility of direct UF as an alternative to conventional pre-treatment (dioxichlorination, coagulation / flocculation, settling and sand filtration) for drinking water treatment plants (DWTPs). Also an optimisation of its performance was conducted after continuously treating during two years raw river water. Several scenarios were addressed, dealing with water of highly variable quality (Table 8.1) and using a full scale module, so that conclusions could be extrapolated for full scale plants.

In particular, in terms of **substitution feasibility** of conventional pre-treatment by direct UF in DWTPs fed by surface water, it can be stated that:

- From a quality perspective, the permeate quality produced by direct UF was generally higher than that from the conventional pre-treatment. In particular, most of the physico-chemical parameters addressed were removed to a larger extent by direct UF than by conventional pre-treatment (95% confidence intervals given): turbidity 99.5±0.1 vs. 97.8±0.4%, TSS 96.2±1.3 vs. 96.3±1.2% and $MFI_{0.45}$ 100.0±0.0 vs. 96.2±2.0%, but DOC: 22.4±5.4 vs. 22.5±4.6% and UV_{254}: 16.8±1.8 vs. 25.0±1.8% reductions were higher in the conventional pre-treatment scheme. From a microbiological standpoint, direct UF proved to be particularly advantageous removing bacterial indicators and human viruses' genome copies, outperforming the conventional pre-treatment. Average physico-chemical and microbiological values of the monitored parameters in the UF permeate, as well as maximum and minimum values in raw Llobregat River are listed in Table 8.1. Microbiological monitored parameters showed the permeate quality to be independent of the incoming water quality fluctuations, producing treated water of constant quality.
- From an operational standpoint, direct UF offered the capability of continuously treating surface water despite the occurrence of extreme events, such as flash floods. Commonly, conventional pre-treatment is stopped when feed water turbidity is above 500 – 1,000 NTU. On the contrary, direct UF was capable of keep treating raw river water, so that the proposed scheme would enable the treatment of water that is not currently used.
- The operational conditions attainable by direct UF differed between seasons. Higher filtration fluxes were achieved in summer (water average temperature 26.5ºC) than in winter (water average temperature 8.9ºC) periods (70 L/(m^2·h) vs. 40 L/(m^2·h) respectively). This could be due to the membrane properties and/or the feed physico-chemical water characteristics. Dissolved organic carbon (DOC) concentration was higher in winter (7.3±3.7 vs. 4.4±0.8 mg C/L), with greater biopolymers (BP) content (1184 vs. 806 µg C/L), which have been claimed to be main membrane foulants (Neubrand et al. 2010). This could explain the differences encountered.
- A greater hydraulic cleaning (HC) efficiency was experienced in winter, so that it is hypothesized that foulants tended to form a looser cake or that lower amounts were accumulated during that season. However, the cake presented higher resistance, leading to larger transmembrane pressure (TMP) increase during filtration. This is in accordance with the lower sustainable fluxes attainable in winter, because TMP was limited to 1 bar. The

hypothesis for summer periods is that a more porous cake was formed, which caused a lower pressure drop, but it was probably more tightly bounded to the membrane, provoking a lower HC efficiency. Alternatively, larger amounts of foulants were accumulated which could also provoke lower HC efficiency.

Table 8.1. Raw river water minimum and maximum and UF permeate average concentrations quantified during the two year period tested (data from Chapter 4 and 6). LoQ: limit of quantification, MPN: most probable number, CFU: colony forming units, CFU: plaque forming units, GC: genome copy.

Parameter	Unit	Raw water		UF permeate
		Min	Max	Ave
Turbidity	NTU	5	> 1,000	0.07
TSS	mg/L	< LoQ	4,432	0.92
DOC	mg C/L	2	14	3.8
UV_{254}	cm^{-1}	0.062	0.430	0.082
SDI_{15}	%/min	> 5	> 5	1.9
$MFI_{0.45}$	s/L^2	20.2	19,091.9	0.9
Total coliforms	log(MPN/100mL)	3.11	6.20	Absence
Faecal coliforms	log(MPN/100mL)	2.04	5.38	Absence
E. coli	log(MPN/100mL)	1.70	5.20	Absence
Aerobic bacteria at 22ºC	log(CFU/mL)	3.45	6.47	2.44
Clostridis perfringens	log(CFU/mL)	1.28	4.96	Absence
E. coli	log(CFU/L)	3.00	5.71	<LoQ
SSRC	log(CFU/L)	3.48	5.10	<LoQ
Somatic coliphages	log(PFU/L)	3.81	5.45	0.43
F-specific RNA coliphages	log (PFU/L)	2.30	4.56	0.04
Infectious enteroviruses (ENT1)	log(PFU/L)	<0.20	0.62	-2.96
Genome copies of enteroviruses (ENT2)	log(GC/L)	3.30	5.77	0.67
Noroviruses of genotype I (NoV GI)	log(GC/L)	2.90	6.03	0.03
Noroviruses of genotype II (NoV GII)	log(GC/L)	3.13	5.83	0.03

Regarding membrane **fouling**, which is a main concern that limits the wider implementation of membrane based processes, it can be concluded that:

- A micro-coagulation (dose < 1.5 mg/L as Fe (III)) prior to the UF alleviated the fouling suffered by direct UF. It enabled an increase in the filtration flux attainable in winter, from 40 $L/(m^2 \cdot h)$ to 70 $L/(m^2 \cdot h)$, a decrease in the specific cake resistance (6 fold approximately) and a stabilisation of the latter (standard deviation diminished 180 fold approximately). In summer, despite the fact that the attainable flux reminded the same with and without micro-coagulation (70 $L/(m^2 \cdot h)$), the specific cake resistance was lowered 2.5 times and was stabilised as well. The effects experienced could be due to the formation of a more porous

cake when micro-coagulation was in place, leading to a lower hydraulic resistance increase during filtration.

- The micro-coagulation reduced by 50% the cleaning operations' frequency approximately in all the conditions addressed and improved the efficiency of the hydraulic cleanings. This could be explained by the characteristics of the fouling layer created, more easily removable by physical means.
- The degree of fouling reversibility depended on the hydraulic cleaning related variables: the more intensive a backwash was the more effective it was in removing foulants from the membrane. Among all cleaning agents evaluated, NaClO performed the best at enhancing fouling reversibility for the considered water.
- Among all organic fractions, UF membrane preferentially retained the heavier BP, followed by intermediate humic substances (HS) and lighter (and smaller) building blocks (BB) and low molecular weight neutrals (LMWN). Successive backwashes (BW) and chemical cleanings in place (CIP) resulted in the detachment of a significant percentage of the retained BP whereas only a modest percentage of the retained HS.

Another concern of membrane processes is their ageing and the effects that this can provoke in terms of **membrane integrity** and thus, the quality of the permeate produced. This is due to the fact that UF removal capacity mainly relies on the sieving effect of its pores, retaining those compounds / microorganisms larger than the pore size. However, if membrane integrity is compromised its removal capacity cannot be guaranteed. Direct UF represents a challenging position due to the lack of previous unitary processes; as a result, the membrane integrity becomes particularly important. In this regard, it can be derived that:

- A protocol capable of assessing membrane integrity by microbes' based assays at pilot scale for the three existing UF hollow fibre configurations (whose pore sizes were 20, 30 and 40 nm) was successfully developed and implemented. Bacteriophage PDR-1 (60 - 70 nm in size) and *Bacillus* spores (length > 1,000 nm and diameter > 500 nm) appear as suitable microbes to monitor UF membrane integrity. Bacteriophage PDR-1 is easier to grow to higher densities than *Bacillus* spores and therefore it may be a better option in some cases. However, obtaining sufficient amounts of phages to seed a full water treatment process is still challenging.
- The analysis of the monitored microbiological data indicated that any perceptible loss of integrity of the tested membrane on direct UF scheme did not occur during the 2 years of continuous operation.
- Both naturally occurring viral indicators studied (somatic coliphages and F-specific RNA bacteriophages) were removed by direct UF similarly to human viruses when measured as genome copies (GC), and similarly to seeded small bacteriophages (GA and MS-2). They can be suggested to be used to follow up the performance of UF membranes in terms of virus removal. Taking into consideration the large numbers found in the raw river water and in the permeate, as well as the straightforwardness of the standardised enumeration method (ISO, 2000), somatic coliphages (SOMCPH) could be considered as a suitable tool for surveying the performance of UF membranes with indicators present in the raw river water. In this case, reductions between 3.0 and 4.0 $\log_{10}$ units of the numbers of somatic coliphages would be expectable.

Concerning additional **impacts** of implementing direct UF on a subsequent **RO unit**, it can be concluded that:

- The increased quality of the UF permeate compared to the conventional pre-treatment in terms of turbidity, total suspended solids, SDI_{15} and $MFI_{0.45}$ may lead to less fouling on the subsequent RO unit. This in turn would lower the cleaning reagents needs, the process downtime and ultimately increase the RO membrane lifetime.
- The implementation of direct UF enables the avoidance of an initial dioxichlorination. In order to guarantee that chlorine based products (mainly from the dioxichlorination, but also from the hypochlorite used in the UF CEBs) do not reach the RO membrane, bisulphite is dosed. The reaction between bisulphite and Fe(III) was shown to be detrimental to the RO membranes' integrity, since their chloride passage and water flux increased quickly under the conditions tested. These transport properties changes were caused by an increase in the fraction of aggregate pores and in the size of network pores of the RO membrane, but the polyamide bond was not broken. No major changes in terms of membrane composition were quantified.
- The implementation of direct UF also enables the minimisation or the avoidance of coagulants dosage, such as ferric chloride. Fe(III) enhanced the incorporation of bromine in the membrane in the presence of chlorite and bromide, probably due to the formation of hypobromous acid or bromine. This turned into an increased water flux and chloride passage under the conditions assessed, being the latter a time dependent process, with greater values under longer exposure time.

  Therefore, the direct UF scheme proposed would be advantageous for the subsequent RO membranes in terms of degradation as well.

8.2. Outlook

Further research should focus on i) understanding seasonal and micro-coagulation impact on the UF membrane behaviour; ii) the quantification at pilot scale of the impact of direct UF on a subsequent RO stage; iii) the assessment of the sensitivity of the membrane integrity methods developed with compromised UF membranes and the comparison with alternative assays; iv) studying the reaction paths occurring between bisulphite and Fe(III), and the degradation effects between the generated species and the RO membrane which lead to the performance deterioration of the latter.

The comprehension of the hydraulic performance of the UF membrane under the conditions considered (winter/summer, coagulation/no coagulation) could enable further optimisation of the process operation. Literature has often attributed the UF enhanced performance caused by a preliminary coagulation to a shift of the main fouling mechanism, from pore constriction or blocking to cake layer formation (Huang et al., 2009, Tabatabai et al., 2009). Nevertheless, because a full scale module was used within this thesis some hydraulic conditions could not be applied. Bench scale tests with real water should be performed to identify the main fouling mechanism occurring in each case, to determine if they are responsible for the differences encountered.

DOC proved to be a key parameter driving the membrane behaviour. As a result, DOC fractionation from all the streams (feed, permeate, hydraulic cleaning, CEB basic-oxidising and CEB acid) in all the conditions considered could provide insights into the nature of the main foulants present, retained and released in each case. A UF membrane autopsy could also help understanding the functioning of the membrane and offer additional information on areas of improvement, especially in terms of cleaning operations. As commented, during the two years of continuous operation of direct UF, the parameters related to the HC and the chemically enhanced backwash (CEB) were not modified. Therefore, room for improvement in those variables could exist.

Regarding the advantages of direct UF on the following RO stage, the comparison between cleaning requirements and RO membrane lifetime when a conventional pre-treatment and when direct UF are implemented should be addressed. Studies at pilot level during at least two years with real water would be recommended in order to obtain reliable data. RO membrane autopsies at the end of the project would provide further insights into fouling nature and extent, integrity of the RO membranes and potential failures of each pre-treatment. An engineering study on the full scale implementation of each option with the associated costs, as well as an environmental assessment (e.g. through life cycle assessment) would also provide further insights for plant managers when considering the most convenient pre-treatment scheme for DWTPs.

In terms of UF membrane integrity, more studies could be conducted deliberately compromising membrane integrity and monitoring the presence of the seeded microbes in the permeate stream. This would enable the quantification of the sensitivity of the protocol defined because during the thesis development the assessed UF membrane was not compromised. In addition to this, relationships between the degree of damage caused and the selected microbes' passage could be established, providing further insights into removal warranties. In addition to this, alternative parameters (physico-chemical or microbiological) could be considered in order to determine whereas other assays could provide equivalent information.

Research on the reactions occurring between bisulphite and iron(III) should be explored, to better understand the formation path of the degrading species and their kinetics. Additional advanced characterisation techniques, such as Fourier transformed infrared spectroscopy (FTIR), could be conducted to identify changes in the binding energies of certain functional groups of the RO membrane and thus, comprehend the interaction between the degrading compounds and the membrane and thus, the degradation mechanism taking place. A better understanding of the compounds formation and their interaction with the membrane could enable their formation avoidance/minimisation or the occurrence of their negative effects on the membrane.

A similar study should be conducted with aluminium, because it is commonly used as coagulant as well. Despite membrane manufacturers limit aluminium concentration at RO feed stream, because it could have a catalytic effect analogously to iron(III), even low concentrations could provoke similar reactions and thus, should be explored.